PB84-140169

Fate of Selected Toxic Compounds Under Controlled Redox Potential and pH Conditions in Soil and Sediment-Water Systems

Louisiana State Univ., Baton Rouge

Prepared for

Environmental Research Lab., Athens, GA

Jan 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-140169

EPA-600/3-83-018
January 1984

FATE OF SELECTED TOXIC COMPOUNDS UNDER CONTROLLED REDOX POTENTIAL AND pH CONDITIONS IN SOIL AND SEDIMENT-WATER SYSTEMS

by

Robert P. Gambrell
Barbara A. Taylor
K. S. Reddy
W. H. Patrick, Jr.

Laboratory for Wetland Soils and Sediments
Center for Wetland Resources
Louisiana State University
Baton Rouge, Louisiana 70803-7511

Grant No. R-807018

Project Officer

Harvey W. Holm
Environmental Systems Branch
Environmental Research Laboratory
U. S. Environmental Protection Agency
Athens, Georgia 30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30613

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-84-018	2.	3. RECIPIENT'S ACCESSION NO. PB84 140169
4. TITLE AND SUBTITLE Fate of Selected Toxic Compounds under Controlled Redox Potential and pH Conditions in Soil and Sediment-Water Systems		5. REPORT DATE January 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R.B. Gambrell, B.A. Taylor, K.S. Reddy and W.H. Patrick, Jr.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Laboratory for Wetland Soils and Sediments Center for Wetland Resources Louisiana State University Baton Rouge LA 70803		10. PROGRAM ELEMENT NO. CCBE1A
		11. CONTRACT/GRANT NO. R-807018
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Athens GA Office of Research and Development Environmental Research Laboratory Athens GA 30613		13. TYPE OF REPORT AND PERIOD COVERED Final, 10/79-10/82
		14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A study was conducted to determine the effects of pH and redox potential conditions on the degradation of selected synthetic organics. Also, the effects of these physicochemical parameters as well as other physical and chemical properties of soils and sediment-water systems on the adsorption of selected organics were measured. Compounds used in degradation studies included methyl parathion, 2,4-dichlorophenoxyacetic acid (2,4-D), and Aroclor 154 (a polychlorinated biphenyl formulation). Compounds used in adsorption studies included methyl parathion, 2,4-D, and pentachlorophenol. Soils and sediments used for both the degradation and adsorption studies were selected to include materials having a wide range of physical and chemical properties.

Degradation studies conducted on soil and sediment suspensions amended with the synthetic organics and then extracted and analyzed by gas chromatography showed important redox potential effects on the degradation of methyl parathion and 2,4-D, but not Aroclor 1254. Redox potential was shown to have a significant effect on the adsorption of pentachlorophenol as this compound was partitioned more with the solid phase under oxidized conditions than reduced conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 112
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

Although the research described in this report has been funded wholly or in part by [illegible] United States Environmental Protection Agency through Grant Number [illegible] to Louisiana State University, it has not been subjected to the [illegible] required peer and policy review and therefore does not necessarily [illegible] the views of the Agency and no official endorsement should be inferred.

FOREWORD

Environmental protection efforts are increasingly directed toward preventing adverse health and environmental effects associated with specific compounds or natural or human origin. As part of this laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Systems Branch studies complexes of environmental processes that control the transport, transformation, degradation, fate, and impact of pollutants or other materials in soil and water and develops models for assessing exposures to chemical contaminants.

Two key processes influencing the fate and potential human health or environmental effects of pesticides or other synthetic organic chemicals in soil or sediment-water systems are degradation and transport. In this report, the effects of pH and redox potential conditions on the degradation of selected synthetic organics are examined. The degradation and adsorption studies demonstrated that redox potential has a significant sorption effect and that physicochemical properties are important in the persistence and mobility of selected organics in soils and sediment. This information has potential application in the development of models for predicting chemical fate and impact in the environment.

William T. Donaldson
Acting Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

A study was conducted to determine the effects of pH and redox potential conditions on the degradation of selected synthetic organics. Also, the effects of these physicochemical parameters as well as other physical and chemical properties of soils and sediment-water systems on the adsorption of selected organics were measured. Compounds used in degradation studies included methyl parathion, 2,4-D, and Aroclor 1254 (a polychlorinated biphenyl formulation). Compounds used in adsorption studies included methyl parathion, 2,4-D, and pentachlorophenol. Soil and sediment materials used for both the degradation and adsorption studies were selected to include a wide range of physical and chemical properties.

Degradation studies conducted on amended soil and sediment suspensions extracted and analyzed by gas chromatography showed important redox potential effects on the degradation of methyl parathion and 2,4-D, but not Aroclor 1254. Methyl parathion was removed much more rapidly under reducing conditions. Oxidized conditions contributed to more rapid degradation of 2,4-D. Degradation studies conducted with ^{14}C-labeled compounds also showed important effects of oxidation-reduction conditions on mineralization of the synthetic organics. However, if collection of the labeled carbon as evolved carbon dioxide is the criteria for measuring degradation, the rate of degradation and the treatment effects, in the case of methyl parathion, were found to be very different compared to degradation studies using extraction and gas chromatography for analysis. Differences due to analytical procedures used were discussed in terms of whether one was looking for initial modification of the parent molecule during degradation or mineralization of the ^{14}C-containing portion of a labeled compound. The latter would usually involve a sequence of degradative steps before the label was converted to carbon dioxide.

Redox potential was shown to have a significant effect on the adsorption of pentachlorophenol as this compound was partitioned more with the solid phase under oxidized conditions than reduced conditions. Correlation coefficients between methyl parathion and 2,4-D adsorption and several soil physical and chemical properties were determined. In particular, an effort was made to identify important properties contributing to adsorption in soils and sediments with a low organic matter content.

These degradation and adsorption studies demonstrated the importance of physicochemical properties on the persistence and mobility of selected synthetic organics in soils and sediments. Information of this type should improve the capability to predict the fate and potential impacts of synthetic organics in various environmental compartments. However, additional work should be done to establish the effect of these physicochemical conditions on the rate of degradation under natural conditions.

This report was submitted in fulfillment of Grant No. R-807018 by Louisiana State University under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 20, 1979 to October 19, 1982, and work was completed as of September 30, 1983.

CONTENTS

Abstract iv
Figures vi
Tables x
Acknowledgment xi

1. Introduction 1
    Background 1
    Synthetic Organics Selected for Study 2
    Literature review 2
2. Materials and Methods 13
    Characterization of soil materials 13
    Concentration effects of methyl parathion and 2,4-D on the rate of soil reduction 13
    Degradation studies 14
    Adsorption studies 21
3. Results and Discussion 24
    Properties of soil materials and sediment materials studied 24
    Concentration effects of methyl parathion and 2,4-D on the rate of soil reduction 24
    Degradation studies 38
    Adsorption studies 74
4. Summary and Conclusions 86
    Pesticide concentration effects on the rate of soil reduction 86
    Degradation studies 86
    Adsorption studies 89
5. Recommendations 91

Literature Cited 93

FIGURES

Number Page

1 Methyl (a) and ethyl (b) parathion 3

2 Schematic representation of parathion metabolism via nitro reduction (R) or hydrolysis (H) (Sethunathan, 1973c 4

3 2,4-dichlorophenoxy acetic acid 6

4 One possible adsorption mechanism for 2,4-D 8

5 2,4'-dichlorobiphenyl, one of more than 200 possible PCB isomers 10

6 Laboratory microcosm for incubating soil and sediment suspensions under controlled pH and redox potential conditions 15

7 Biometer flask used for degradation studies with ^{14}C-labeled compounds 20

8 Redox potential levels (Eh) with time in a Crowley soil material amended with varying concentrations of 2,4-D and subjected to flooding 26

9 Redox potential levels (Eh) with time in a Cecil soil material amended with varying concentrations of 2,4-D and subjected to flooding 27

10 Redox potential levels (Eh) with time in a Crowley soil material amended with varying concentrations of methyl parathion and subjected to flooding 28

11 Redox potential levels (Eh) with time in a Cecil soil material amended with varying concentrations of methyl parathion and subjected to flooding 29

12 pH values with time in a Crowley soil material amended with varying concentrations of 2,4-D and subjected to flooding 30

13 pH values with time in a Cecil soil material amended with varying concentrations of 2,4-D and subjected to flooding 31

14 pH values with time in a Crowley soil material amended with varying concentrations of methyl parathion and subjected to flooding 33

FIGURES (continued)

Number Page

15 pH values with time in a Cecil soil material amended with varying concentrations of methyl parathion and subjected to flooding 34

16 The effect of redox potential on the recovery of methyl parathion from a Calcasieu River sediment material incubated at pH 8 39

17 The effect of redox potential on the recovery of methyl parathion from the aqueous phase of a Calcasieu River sediment suspension incubated at pH 8 40

18 The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 7 and 8 ppt salinity 41

19 The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 5 and 8 ppt salinity 42

20 The effect of redox potential on the recovery of methyl parathion from a Hartwell Reservoir sediment material incubated at pH 7 43

21 The effect of redox potential on the recovery of methyl parathion from a Hartwell Reservoir sediment material incubated at pH 5 44

22 The effect of redox potential on the recovery of methyl parathion from a Cecil topsoil material incubated at pH 7 45

23 The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 7 and 25 ppt salinity 46

24 The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 5 and 25 ppt salinity 47

25 The effect of redox potential on the recovery of 2,4-D from a Cecil topsoil material incubated at pH 7 50

26 The effect of redox potential on the recovery of Aroclor 1254 from a Hartwell Reservoir sediment material incubated at pH 6 51

27 The effect of redox potential on the recovery of Aroclor 1254 from a Hartwell Reservoir sediment material incubated at pH 8 52

FIGURES (continued)

Number Page

28 Carbon dioxide production as an indication of relative microbial activity in a methyl parathion-amended Hartwell Reservoir sediment material incubated at four redox potential levels at pH 5.0 54

29 Carbon dioxide production as an indication of relative microbial activity in a methyl parathion-amended Cecil topsoil material incubated at four redox potential levels at pH 7.0 55

30 Carbon dioxide production as an indication of relative microbial activity in an Aroclor 1254-amended sediment material incubated at pH 6 and four redox potential levels 56

31 Carbon dioxide production as an indication of relative microbial activity in an Aroclor 1254-amended sediment material incubated at pH 8 and four redox potential levels 57

32 Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil subsoil material 60

33 Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil topsoil material 61

34 Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Crowley soil material 62

35 Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Hartwell Reservoir sediment material 63

36 Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Lake Providence material 64

37 Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Betis topsoil material 65

38 Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil subsoil material 67

FIGURES (continued)

Number Page

39 Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil topsoil material 68

40 Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Crowley topsoil material 69

41 Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Hartwell Reservoir sediment material 70

42 Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Lake Providence sediment material 71

43 Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Betis topsoil material 72

44 Oxidation effects on degradation of labeled 2,4-D (chain labeled) as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil topsoil material 73

TABLES

Number   Page

1 Gas chromatography parameters for methyl parathion, 2,4-D, and Aroclor 1254 18

2 Selected physicochemical properties of soil and sediment materials 25

3 Soluble plus exchangeable Fe, Mn, and Zn levels on selected sampling dates in two soils amended with varying concentrations of methyl parathion 35

4 Soluble plus exchangeable Fe, Mn, and Zn levels on selected sampling dates in two soils amended with varying concentrations of 2,4-D 36

5 R^2 values for Fe, Mn, and Zn as influenced by soil pH and redox potential 37

6 Notes on carbon dioxide collection studies to indicate relative microbial respiration 58

7 Distribution coefficients for methyl parathion equilibrated with 19 soil and sediment materials 75

8 Distribution coefficients for 2,4-D equilibrated with 19 soil and sediment materials 76

9 Percent organic carbon and distribution coefficients on an organic carbon basis for methyl parathion and 2,4-D in 19 soil and sediment materials 77

10 Means, standard deviation, and coefficient of variation for K and K_{oc} values of methyl parathion and 2,4-D adsorption in 19 soil and sediment materials 78

11 R^2 values for KA and KB for 2,4-D and methyl parathion vs. selected independent variables 80

12 Adsorption coefficients for methyl parathion in soil and sediment materials incubated under controlled pH and redox potential conditions 81

13 Adsorption coefficients for 2,4-D in soil and sediment materials incubated under controlled pH and redox potential conditions 83

14 Adsorption-desorption of PCP from Shell Beach sediment . . . 84

ACKNOWLEDGMENTS

The authors wish to acknowledge Ms. Steffanie Scott for operating the microcosms and analyzing samples early in the project, Ms. Rita Strate for typing and editorial assistance, and Ms. Sherri Stewart for help in processing the data. Also, we are grateful to a number of student assistants who washed glassware and ground soil and sediment samples.

SECTION 1

INTRODUCTION

BACKGROUND

The threat of adverse environmental impacts associated with organic pesticide residues or industrial waste depends on several factors. These include: (1) the particular compounds present, (2) the concentrations of the compounds present, (3) the environmental compartments in which the materials are found and the organisms exposed, (4) the persistence or rate of degradation of the material in various environmental compartments, and (5) the transport of the material in the environment. Degradation and transport are two key processes influencing the fate and potential environmental or human health impacts of synthetic organics in soil or sediment-water systems.

A substantial amount of research has been conducted on the degradation and transport of synthetic organics in the last 20 years. However, much of this work has been limited to insecticides and herbicides in typical agricultural soil materials. Until recent years, little work had been done with sediment-water systems or with industrial organics. The sediment-water systems of streams, rivers, lakes, and coastal waters have been major recipients of pesticide residues, industrial organic wastes, and chemicals from transportation accidents (point and nonpoint sources). The physicochemical properties of sediment-water systems affecting the degradation and transport of synthetic organics are often substantially different than the properties of agricultural soils in the area. In deep or quiescent sections of a sediment-water system, the sediments will tend to have a greater clay content, greater humic material content, and strongly anaerobic conditions prevailing in the bulk of the sediment material. However, the oxidation-reduction conditions of suspended particulates and the top few millimeters or centimeters of sediments are aerobic. The microbial and chemical processes occurring in oxidized sediments that may influence the degradation of synthetic organics are similar to processes occurring in typical upland soils. Thus sediment-water systems usually include a wide range of oxidation-reduction conditions.

It has been reported for more than a decade that the degradation rate of some synthetic organics is affected by physicochemical conditions of their environment such as pH, oxidation-reduction intensity, and salinity. However, relatively little research has been done on this topic. Some researchers have made the generalization that the degradation of synthetic organics is faster under anaerobic conditions. The research conducted by this Laboratory over the last few years indicate the effect of oxidation-reduction conditions on degradation rates is very compound specific. Even within the same chemical class (organophosphate insecticides, for example), we have seen one compound degrade more quickly under aerobic conditions while the recovery of another will decrease most rapidly under anaerobic conditions. Because of the recent emphasis on modeling the fate of synthetic organics in the environment and the wide range of physical, chemical, and microbial properties encountered in soils and sediment-water systems that may affect the persistence of synthetic organics, it is important to understand the effects of physicochemical conditions on the degradation of pesticide residues and industrial organic wastes.

It is well established in the literature that soil and sediment humic material is a primary component associated with the adsorption of synthetic organics. Humic materials are also qualitatively and quantitatively affected by oxidation-reduction conditions. Recent literature has clearly demonstrated the partitioning of hydrophobic organics between bound and dissolved forms is associated with the amount of humic materials present. However, the possibility also exists that oxidation-reduction conditions affect the chemical properties of humic materials affecting adsorption of synthetic organics. Other soil components such as hydrous iron oxides that may influence the adsorption of synthetic organics are also affected by oxidation-reduction conditions. One objective of this project was to conduct preliminary investigations into oxidation effects on adsorption.

The objectives of this research were to: (1) determine the effects of pH and oxidation-reduction conditions on the degradation rate of selected toxic synthetic organic compounds, (2) to examine the effects of oxidation-reduction conditions and other soil properties on the adsorption of the selected synthetic organics, and, (3) to demonstrate an experimental approach for evaluating the effects of physicochemical conditions of soil and sediment-water systems on the environmental chemistry of synthetic organics.

SYNTHETIC ORGANICS SELECTED FOR STUDY

The compounds selected for study included methyl parathion (O, O-Dimethyl-O-p-nitrophenyl phosphorothioate), an organophosphorus insecticide; 2,4-D (2,4-Dichlorophenoxyacetic acid), a chlorinated hydrocarbon herbicide; and Aroclor 1254, one formulation of a mixture of variously chlorinated biphenyl compounds where the chlorine content is about 54 percent by weight. Methyl parathion and 2,4-D are pesticides that have been widely used for years and continue to be important chemical pest control agents. Aroclor 1254 is an industrial organic liquid widely used for its non-flammability and for its electrical insulating properties. The PCB's, of which Aroclor 1254 is one formulation, are noted for the large quantities that have been produced and released in the environment, their persistence in the environment, and the health risks of these materials when found in drinking water or food supplies. Another compound, PCP (Pentachlorophenol) was included for adsorption studies only.

LITERATURE REVIEW

Methyl Parathion

The persistence and accumulation of chlorinated hydrocarbon insecticides such as DDT in the environment has led to the use of less persistent insecticides such as the organophosphates. Though more readily degraded than chlorinated hydrocarbon compounds, this compound is relatively more resistant to chemical hydrolysis compared to other organophosphates.

There are two kinds of parathion, both of which are used extensively. Both have a similar structure except for the methyl and ethyl groups. They are: 1) Ethyl Parathion (0, 0, diethyl-0-p-nitrophenyl phosphorothioate) and 2) Methyl Parathion (0, 0, dimethyl-0-p-nitrophenyl phosphorothioate). Methyl parathion has a water solubility of about 60 ppm as compared to the ethyl parathion solubility of 25 ppm, and a vapor pressure of 37.8 mm Hg (Weber, 1972). The structures of ethyl and methyl parathions are given in Figure 1 below:

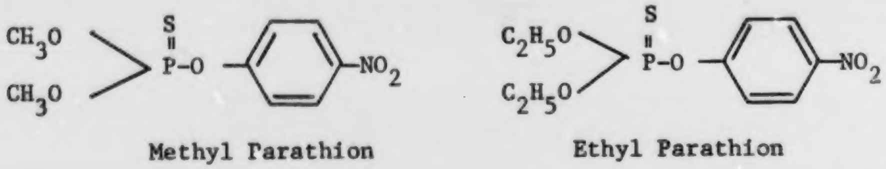

Figure 1. Methyl (a) and ethyl (b) parathion.

Most of the research done on parathion has been with the ethyl form. Hence the literature reported here is mostly on ethyl parathion. Though certainly not identical, the environmental chemistry of these two compounds is somewhat similar. It appears that parathion residues on the soil surface degrade quickly, however, if the residues penetrate into deeper soil layers, the residues are more stable. Toxic residues can be transported to the edible parts of crops. Surface water can also be contaminated if soil particles containing adsorbed parathion residues are transported by runoff water (Nicholson et al., 1962). Since the organophosphates are more water soluble than the chlorinated hydrocarbons, transport of both soluble and adsorbed forms may contribute to surface water contamination. Wershaw and Goldberg (1972) reported that processes affecting the mobilization and immobilization of parathion include: 1) adsorption through H-bonding, 2) adsorption through van der Waal's forces, 3) solubilization reactions, 4) chemisorption, 5) ion exchange, and 6) other chemical reactions. Humic and fulvic acids are the most active components of soil organic matter influencing the fate of parathion. Several functional groups present in humic and fulvic acids appear to interact with parathion.

There is limited information on the degradation pathway of methyl parathion, but there are several studies on the ethyl parathion degradation pathway in flooded and non-flooded soils. Figure 2 shows the proposed pathway of parathion metabolism in flooded soils. As indicated in the schematic below, there are two pathways involved in the biodegradation of parathion: 1) nitrogroup reduction of parathion as occurs in non-flooded and flooded soil systems or in microbial cultures (Lichtenstein and Schulz, 1964; Zuckerman et al., 1970; Sethunathan and Yoshida, 1973) and 2) hydrolysis of parathion to p-nitrophenol as an

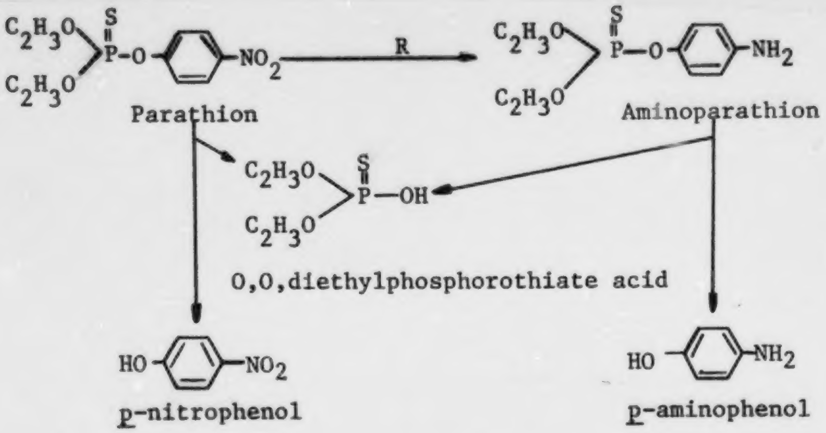

Figure 2. **Schematic representation of parathion metabolism via nitro reduction (R) or hydrolysis (H) (Sethunathan, 1973c).**

intermediate degradation product in a flooded soil (Sethunathan and Yoshida, 1972).

Oxidation and hydrolysis are the most important mechanisms of chemical degradation of parathion. Oxidation of parathion at the P = S bond has been reported to occur under ultraviolet light and in most common oxidation systems. But Lichtenstein and Schulz (1964) and Miyamoto et al. (1966) reported that the chemical oxidation of parathion in soils and waters is not significant. Ahmed et al. (1958) reported that the reduction reactions were more important than the oxidation reactions in metabolizing organophosphate compounds such as parathion.

Sethunathan (1973a) reported that the rate of parathion degradation in soil depends on soil properties. It appears parathion degrades faster in soils that have higher organic matter contents. It was reported to degrade rapidly in acid sulphate soils that had the highest organic matter content of several soils studied, but slowly in lateritic and alluvial soils with low organic matter content. Generally organic materials appear to accelerate the reduction of the nitrogroup in parathion. Rajaram and Sethunathan (1975, 1976) reported the influence of several organic carbon sources on the degradation of parathion in the following order: glucose > rice straw > algal crust > farmyard manure. In soils inoculated with a parathion-hydrolyzing enrichment culture, organic amendments appear to inhibit hydrolysis of parathion - the rate of hydrolysis with different organic matter amendments following a reverse order of that of nitrogroup reduction.

Sethunathan (1973) reported that the addition of rice straw as a source of organic matter inhibited the hydrolysis of parathion to aminoparathion. He also reported rapid transformation of parathion into aminoparathion and an unidentified metabolite in the first 3 days. This was because of a rapid decrease in the redox potential of soil after the addition of organic matter. Sethunathan and Yoshida (1973) reported that parathion degrades faster in near neutral pH soils under flooded conditions than under non-flooded conditions.

Generally, organophosphates are relatively non-persistent. However, Graetz et al. (1970) reported the rate of hydrolysis of parathion in slightly acid lake sediment as 0.15 to 0.18 percent of added parathion per day. This indicates that parathion is very resistant to degradation under acidic conditions (Suffet and Faust, 1972), whereas the hydrolysis rate in calcareous sediments appear to be more rapid. Stewart et al. (1971) reported that 0.1 percent of applied parathion remained in soil even after 16 years because of the association of parathion in lipids of soil organic matter which apparently offered some protection from bacterial degradation and hydrolysis. Lichtenstein and Schutz (1964) reported that the methyl parathion was more readily degradable than ethyl parathion. Under laboratory conditions, nearly 95 percent of applied methyl parathion and 30 percent of applied ethyl parathion were lost within 12 days in a loam soil.

Parathion appears to be more persistent in estuarine water than in soil. Walker (1976) reported that nearly 94 percent of added parathion remained in estuarine water even after 25 days of incubation. Salinity was reported to affect the degradation of organophosphate insecticides like malathion - the degradation rate increasing with an increase in salinity. On the other hand, the degradation rate of parathion may be retarded by increases in salinity. Even after 129 days incubation at a salinity of 40 parts per thousand and at a pH of 8.1, only 45% of the added parathion was lost.

Clay minerals and organic matter are the main soil components that affect the behavior of parathion in the soil environment. The adsorption of parathion on the clay surface is affected by the saturating cation. The sorption sequence for parathion is Li > Al > Mg > Na > K > Ca (Yaron, 1978). Adsorption of parathion is also affected by the type of clay, hydration status of the mineral, and the temperature. Parathion adsorption on clay minerals in a hydrated form decreases with an increase in temperature. The effect of temperature is due to an increase in the solubility of parathion with an increase in temperature, and also due to the fact that desorption, being an exothermic process, will decrease with increasing temperature. Yaron (1978) reported that in a partially hydrated-attapulgite system, parathion molecules cannot replace the strongly adsorbed water molecule, such that parathion adsorption occurs on water-free surfaces only. This led to the decreased adsorption of parathion on attapulgite. The clay-parathion complex is coordinated through cations, the type of cation determining the structure of the complex.

Clay surfaces appear to catalyze the degradation of parathion. Yaron (1978) reported that Kaolinite enhances the degradation of parathion, which is mainly moisture and cation-dependent. He further reported relative parathion degradation was 93 percent for Ca-saturated clays and 16 percent for Na and Al-Kaolinites. Whereas for methyl parathion, the degradation was 64 percent for Ca-saturated clays, and less than 15 percent for Na and Al-Kaolinites. Finely et al. (1977) studied the absorption of methyl parathion by clothes worn by workers in the cotton field sprayed with this insecticide. It appears that all-cotton clothing absorbs less methyl parathion as compared to cotton-polyester blends.

Rajaram and Sethunathan (1976) reported that certain toxic products produced (Patrick, 1971) during the decomposition of organic matter appear to block hydrolysis of parathion in rice-amended soil under flooded conditions. These toxic substances produced were not inactivated by heat treatment of the soil.

Several microorganisms are responsible for the degradation of parathion in soils and sediments (Sethunathan, 1973b). Lichtenstein and Schulz (1964) reported that a yeast was capable of degrading parathion. Miyamoto et al. (1966) studied the major degradative pathway of methyl parathion incubated with the bacterium *Bacillus subtilis*. This resulted in the reduction of methyl parathion to an amino compound and then hydrolysis to dimethylphosphorothioic acid. Zuckerman et al. (1970) reported parathion metabolized into four compounds, the major metabolite being aminoparathion. Rao and Sethunathan (1974) reported that a fungus *Pencillium walksmani* Zaleski degraded parathion in acid sulphate soil under flooded conditions. This fungus was reported to be very tolerant to high concentrations (1000 ppm) of parathion. In flooded soils that become predominantly anaerobic within a few days after flooding, the facultative anaerobe *Flavobacterium sp*. decomposes parathion.

2,4-D

The herbicide 2,4-D (2,4-dichlorophenoxy acetic acid) is one of the most widely used chemicals for weed control (Figure 3). Extensive research has been conducted on its fate and behavior in soil-plant systems (Newman et al., 1952; Ogle and Warren, 1954; Harris and Warren, 1964; Wiese and Davis, 1964; Lavy et al., 1973; CAST, 1975). Its chemical structure is given below. It has a molecular weight of 222, and a water solubility of about 650 ppm. This compound and its esters are also widely used for controlling some species of aquatic weeds in lakes, ponds, and reservoirs.

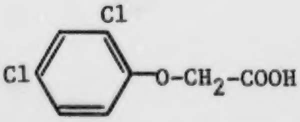

Figure 3. 2,4-dichlorophenoxy acetic acid.

Residues of 2,4-D in water can come from several different sources including: 1) runoff water from agricultural and non-agricultural land, 2) drift from aerial or ground applications, 3) applications to control floating, submerged and marginal aquatic vegetation, 4) control of ditchbank vegetation, 5) emptying and washing of herbicide application equipment, and 6) discharge of industrial wastewater (Frank, 1972). Residues of 2,4-D may accumulate in soils as spray, either directly to the soil surface or as the material on aerial parts of plants drip from the leaves on to the soil surface, or, as a result of the decay of weeds to which 2,4-D was applied.

Residues of 2,4-D that reach the soil from leaves and from direct application are tightly bound to several adsorptive soil components and thus are usually found in the upper part of the soil. The adsorption of herbicides by soil humus and clay colloids causes some difficulties in assessing their long-term fate in soils and sediments. The herbicides adsorbed on soil particles may be transported by soil erosion to lakes or reservoirs and may persist there due to unfavorable conditions for microbial degradation. Thus the strong adsorptive properties of soils and sediments as well as degradation rates under different physicochemical conditions must be considered to evaluate the impact and fate of herbicide residues.

It appears that the adsorption of 2,4-D by soil colloids can reduce its effectiveness and mobility (Crafts, 1960), resulting in the reduction of leaching of 2,4-D into groundwater. But the 2,4-D sorbed on soil particles can be carried into surface waters by erosion of contaminated soil particles. The adsorbed 2,4-D may eventually desorb and contaminate surface waters.

Leaching and movement of a herbicide like 2,4-D are affected by the solubility of the herbicide, adsorption of herbicide on the soil, moisture level of the soil at the time of application, and the amount of evaporation between rains (Hartley, 1960). The rate of leaching of 2,4-D is also influenced by soil organic matter, being leached more in soils low in organic matter than in soils of greater organic matter content (Hernandez and Warren, 1950). The molecular weight of the herbicide and the type of salts likely to be found in the soil also influence leaching. Residues of 2,4-D have been reported to leach readily in a sandy soil and very slowly in a muck soil.

The 2,4-D molecule is a weak acid with a dissociation constant, Kd, of about 10^{-4} (Haque and Sexton, 1968). This acidic herbicide can readily dissociate in solution to form anionic species. In aqueous solution, both the dissociated and undissociated species exist. The proportion of each species depends on the pH of soil solution. The dissociated anions are not readily adsorbed directly by the negatively charged soil colloids. Weber (1970) reported that these organic anions may be adsorbed by positively charged oxyhydroxides of iron and aluminum through anion-exchange reactions. He also reported that the phenoxy herbicides may precipitate as calcium salts in calcareous soils. These processes appear to reduce the mobility and effectiveness of 2,4-D.

The 2,4-D molecule can be bonded to several soil colloids through the aromatic rings and functional groups. The adsorption strength appears to be weaker for an acidic herbicide like 2,4-D than for basic herbicides such as triazines (Weber et al., 1965). Reactions of the following type may be responsible for adsorption of 2,4-D on an anion-exchange site such as ferric oxyhydroxides (Figure 4).

Miller and Faust (1972) reported that even though clays are negatively charged, they can indirectly adsorb the negatively charged 2,4-D molecules.

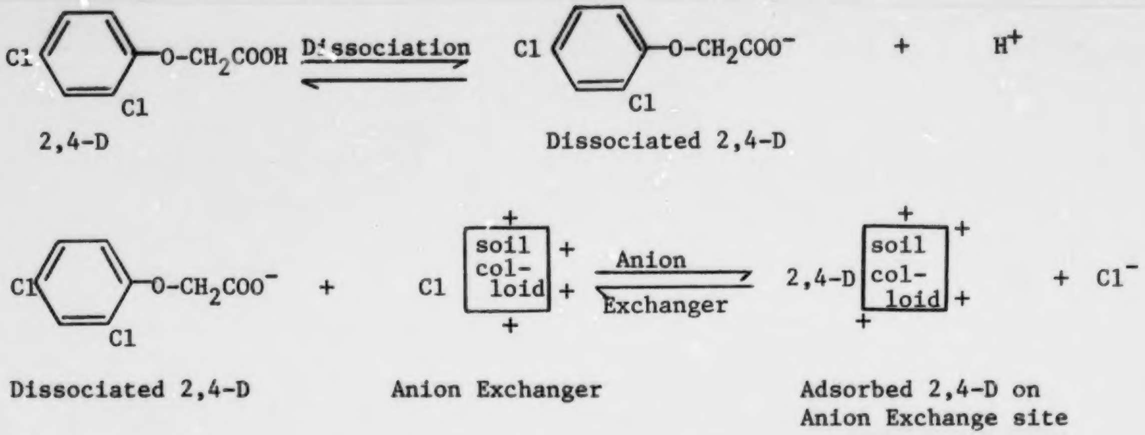

Figure 4. One possible adsorption mechanism for 2,4-D.

It appears clays adsorb soil organic molecules in a specific orientation and the resulting soil organic matter coated clays then adsorb 2,4-D. They also reported that several industrial wastes such as cationic detergents, disinfectants, cationic dyes, floatation chemicals, and various anions bond to clays strongly, thereby forming an organic surface on which organic molecules such as 2,4-D can sorb. Miller and Faust (1972) reported that the sorption of 2,4-D by Bentone-24 (Wyoming bentonite coated by sorbed dimethylbenzyl octadecyl ammonium chloride) increases with an increase in clay:water ratio and a decrease in pH from 7.0 to 3.4. Sorption was also affected by the type of cation present.

Harris and Warren (1964) reported the adsorption of 2,4-D by an organic muck soil, bentonite, an anion-exchanger and a cation-exchanger. Their results show that the adsorption depends upon several factors including the nature of adsorbent, pH, temperature, and the nature of herbicide. Their results also show that 2,4-D was readily desorbed from bentonite compared to a muck soil. These findings suggest that 2,4-D is more strongly adsorbed by organic matter than by clay minerals like bentonite. Weber (1972) reported that 2,4-D is adsorbed on these compounds in molecular form under acidic conditions. The adsorption mechanisms for the anionic herbicides in acidic medium involve hydrogen bonding with multiple sites being available on the surfaces of both organic matter and herbicide. Whereas under neutral or alkaline soil conditions, the anionic herbicides are bound through salt linkage (Stevenson, 1972; Khan, 1973).

The two major types of adsorbing surfaces available for herbicides are the clay-humus surface and clay surface alone. The relative contribution of humus and clay to the adsorption of 2,4-D depends upon the extent of coating of clay minerals by humus. Stevenson (1972) reported that if the soil contains more than 8 percent organic matter, the organic surfaces are primarily responsible for adsorption of herbicides. The clay minerals are mainly responsible for the adsorption of herbicides in soils containing less than 8 per cent organic matter. But in soils with similar organic matter content, the contribution of humus to the adsorption of herbicides will be more than the clay where Kaolinite is the predominant clay mineral, and less than the clay where montmorillonite is the predominant clay mineral. Adsorption capacity for three dominant clay minerals in soils follows the order: montmorillonite > illite > kaolinite.

Acidic herbicides like 2,4-D and 2,4,5-T may leach readily in coarse textured soils and in soils low in organic matter (Ogle and Warren, 1954; Wiese and Davis, 1964; Weber, 1972; White et al., 1976). Several bonding mechanisms such as H-bonding, ion exchange, van der Waal's forces and coordination through the attached metal ion (salt linkage) are responsible for the adsorption of herbicides by soil colloids. But for anionic herbicides like 2,4-D, H-bonding and salt linkage are especially important (Stevenson, 1972).

The adsorption of 2,4-D depends upon several factors like temperature, solubility of the compound, moisture content and other surface properties of soil colloids. Since the adsorption process is an exothermic reaction, it decreases with increasing temperature. Temperature also affects the adsorption indirectly by its effect on the solubility of 2,4-D. The type of cation associated with 2,4-D affects its solubility and hence its adsorption. Aly and Faust (1964) reported the solubility of calcium salt of 2,4-D as 4000 mg/ℓ, and that of magnesium salt of 2,4-D as 11,000 mg/ℓ.

The degradation of 2,4-D has generally been attributed to microbial activity. Soil and environmental factors which can affect microbial activity could also influence 2,4-D degradation indirectly. Persistence of 2,4-D has been reported to vary from 10 days to 14 weeks. The variations in persistence are attributed to different soil types, rainfall, temperature, application rates, formulations, and other factors. Brown and Michell (1948) reported that a low moisture content of 5 to 10 percent or below, and a low soil temperature of about 50°F prolong the toxic effects of 2,4-D in soils. It also persists for a long period of time under field conditions in cold weather. Factors such as soil organic matter content, soil moisture, and temperature apparently influence the rate of 2,4-D inactivation indirectly through their effect on the growth of soil microorganisms. The breakdown of 2,4-D is also affected by soil type. Ogle and Warren (1954) reported the degradation of 2,4-D was lowest in sandy soil, intermediate in silt loam, and highest in muck soil. Bioactivity, persistence, biodegradability and leachability have been found to be directly related to the humus content of the soil (Bailey and White, 1964).

Bell (1956) reported that photodegradation is not the major route of dissipation of 2,4-D in soil. Andus (1964) discussed in detail the behavior of herbicides in soil. Research done in the past indicates that biodegradation is mainly responsible for its dissipation.

Crafts (1964) reported that metabolism by plants also contributed to the disappearance of 2,4-D from soil. The bacterium *Sporocytophaga congregata*, an obligate aerobic organism has been shown to be effective in degrading 2,4-D in soil under aerobic conditions (Jensen and Peterson, 1952). Lavy et al. (1973) reported rapid dissipation of 2,4-D under both aerobic and anaerobic conditions in the soil. This, they attributed to the presence of facultative microorganisms.

From the literature available, it is apparent that both the adsorption and degradation of 2,4-D in soils and sediments must be considered in evaluating its fate and environmental impact.

Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls, usually called PCBs, consist of two benzene rings joined with a C-C bond between one carbon atom of each ring, and up to 10 chlorine substitutes for hydrogen on the rings (Figure 5). Considering the varying number and positions of possible chlorine substitutions, there are more than 200 possible compounds or isomers. PCBs were produced as mixtures of various isomers, thus they are found in the environment as mixtures of isomers. PCBs have been manufactured since 1929 and it has been estimated that total production has exceeded 800 million pounds before their manufacture ceased in the U. S. in the late 1970s. Because PCBs are non-flammable fluids (if there are four or more chlorine substitutions) with excellent dielectric properties, they have been widely used in the manufacture of countless industrial and consumer items. Some of the industrial applications include high pressure and temperature lubricants, hydraulic fluids, plasticizers, heat transfer and electrical insulation fluids, and others (Griffin et al., 1977).

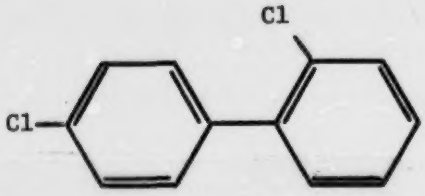

Figure 5. 2,4'-dichlorobiphenyl, one of more than 200 possible PCB isomers.

Although there are now restrictions on the uses of PCBs, its persistence coupled with accidental releases, waste discharges, and improper disposal of old equipment has resulted in its widespread distribution in the environment. Transport of PCBs can be from industrial sources and other contaminated areas by streams and rivers or by atmospheric movement (Armstrong and Swackhamer, 1982). The importance of atmospheric transport is indicated by results of a study suggesting atmospheric transport and subsequent deposition may be the primary input mechanism for PCB into Lake Superior (Eisenreich et al., 1979).

Because of their widespread distribution in the environment, their toxicity to aquatic organisms and man, and their persistence, there is much interest in the rate of degradation of PCBs in different compartments of the environment as well as in factors affecting degradation. Degradation of PCBs in soils and sediment-water systems occurs primarily either by microbial action or photochemical pathways, the photochemical route being the only significant non-biological degradative pathway. Photochemical degradation may be a factor for a portion of the trace levels of PCBs dissolved in shallow surface waters, suspended on particulates in shallow reaches of surface waters, or moving by atmospheric transport during air transport. However, much of the PCB contamination of the environment is associated with sediments where photodegradation is not an effective dissimulative mechanism. In sediments and all but the very surface layer of soils, microbial degradation will be the primary degradative mechanism.

PCBs are strongly adsorbed to the sediment solid phase, but there is some low level of PCBs in the aqueous phase, though the concentrations are very low (Fulk et al., 1975). However, the fact that most of the PCBs are bound with the sediment phase does not mean that the PCBs no longer represent an environmental or health threat. When PCB contaminated sediments have been introduced into an uncontaminated sediment-water system, high levels of PCBs have accumulated in fish indicating transport by one or more processes from the sediment phase (Sherwood, 1976).

Pure culture studies have demonstrated the potential for PCB degradation by microorganisms. It has been reported, using pure culture techniques, that bacteria capable of degrading PCBs were present in all of numerous water and sediment samples taken from many areas of the east coast of the United States (Sayler et al., 1978). The more contaminted areas had greater numbers of PCB degrading bacteria and a greater diversity of organisms capable of degrading PCBs.

Both the position of chlorine substitution and the number of chlorine substitutions on a biphenyl ring have been reported to affect microbial degradation rates. Wong and Kaiser (1974) reported the order of degradation rates of biphenyl and two mono-chloro isomers as biphenyl > 2-chlorobiphenyl > 4-chlorobiphenyl.

Shiaris and Sayler (1982) reported a natural, mixed population of microorganisms in lake water could oxidize 2-chlorobiphenyl, but not 2,4'-dichlorobiphenyl. The number of chlorine substitutions is probably a more important factor affecting degradation rate. Veight (1970) noted that Aroclor 1242 levels decreased faster in surface waters than Aroclor 1260 and suggested Aroclor 1260, which has greater chlorine substitution, was more persistent. In a study with one microbial genus, Gibson et al. (1973) found that biphenyl and monochlorinated derivations of Aroclor 1221 were degraded more rapidly than the more highly chlorine substituted isomers. Others have also reported that increasing chlorination levels result in greater persistence of biphenyl (Ahmed and Focht, 1973; Tucker et al., 1975).

Most PCB degradation work has been done with pure cultures under oxidized conditions. The relatively little work done on natural systems suggest PCBs may be more resistant under anaerobic conditions. Fries (1972) reported no apparent degradation of Aroclor 1254 in silage subjected to typical anaerobic fermentation for several months. Labeled tetrachlorobiphenyl has been incubated with reduced marsh soil and sea water for 45 days with no apparent transformation of the original molecule, though some degradation was measured within 10 days under aerobic conditions (Carey and Harvey, 1978). Johnson (1973) incubated soil and cattle manure-enriched soil with selected single PCB isomers under flooded conditions for one month and reported no degradation was observed.

Griffin et al. (1978) reported aerobic degradation of water soluble Aroclor 1242 was 92 percent complete within 1 day and that isomers with less than four chlorines were degraded while those with four or more chlorines did not degrade to a significant extent. In view of this apparent rapid degradation rate, two things should be pointed out: 1) the water soluble Aroclor 1242 may have been predominately the isomers with the least chlorine substitution that are known to degrade most quickly, and, 2) the amount of water soluble PCB in a typical contaminated sediment-water system represents a very small proportion of the total. In field plots where PCB-contaminated sewage sludge had been applied for 7 years, the PCBs recovered were primarily the high chlorine substituted isomers.

SECTION 2

MATERIALS AND METHODS

CHARACTERIZATION OF SOIL MATERIALS

Soil and sediment materials were air-dried and ground to pass through a 2 mm sieve for characterizing selected physical and chemical properties. Soil samples were characterized for pH, cation exchange capacity, organic carbon, particle size distribution, free iron oxides, and Ca, Al, and Mn extracted with the free iron oxides. Sample pH was determined on a 1:1 soil-water suspension (Peech, 1965). Cation exchange capacity was determined by the ammonium acetate method (Chapman, 1965). Organic carbon was determined by the Walkley and Black method (Jackson, 1967), and organic matter content was calculated by multiplying organic carbon by a factor 1.724 (Wilson and Staker, 1932). The particle size distribution was determined by the hydrometer method (Day, 1965), and free iron oxide was extracted by an ammonium oxalate extraction procedure (McKeague and Day, 1966). Iron, Al, Ca, and Mn were measured in the ammonium oxalate extract by an ICP emission spectrometer.

CONCENTRATION EFFECTS OF METHYL PARATHION AND 2,4-D ON THE RATE OF SOIL REDUCTION

The insecticide methyl parathion (0,0-dimethyl-0-p-nitrophenyl phosphorothioate) and the herbicide 2,4-D (2,4-dichlorophenoxy acetic acid) were used in this study. Two surface soil materials were used: a Crowley silt loam and a Cecil clay loam. Five concentration levels were studied: 0, 5, 10, 25, and 75 µg/g, oven dry solids basis. To simulate the flooded soil system in the laboratory, 10 g aliquots of air-dried and ground soil amended with specified concentrations of the two compounds were placed in test tubes and 15 ml of deionized water was added to flood the soil. A fresh sample of bayou water containing a small quantity of bottom sediment was collected, mixed well, and allowed to settle. One-half ml of the supernatent was then added to each test tube to innoculate the soil-water mixtures, then the tubes were shaken and allowed to settle. Eighty tubes were used for each compound (8 sampling dates x 2 subsamples x 5 concentration levels). Replicate subsamples were taken for measurements at 0, 2, 4, 6, 9, 12, 16, and 20 days for methyl parathion and 0, 6, 12, 18, 24, 30, 40, and 50 days for 2,4-D. Temperature was maintained at 28°C C±2°. The test tubes were sealed and were purged with nitrogen once a day.

Redox potential was measured by placing bright platinum electrodes in the soil material in those tubes removed for sampling. A measurement was recorded after allowing one hour for equilibration of the electrode in the soil.

Soil pH was measured using a calibrated, combination pH electrode that was inserted directly into the soil material.

Exchangeable metals were extracted by shaking the soil materials with 30 ml of a 1N ammonium acetate solution for one hour (15 mls of 2N ammonium acetate were added to the soil-water mixture, as described by Howeler and Bouldin, 1971). The pH of the ammonium acetate solution was adjusted to approximately the pH of the soil-water mixture. After shaking, the soil suspensions were centrifuged at 2,000 rpm for 10 minutes (IEC #277 rotor) and then filtered. Extractable Fe, Mn, and Zn were measured by an ICP emission spectrometer. This extraction would include both water soluble and exchangeable metals.

DEGRADATION STUDIES

Controlled pH-Redox Potential Microcosms Using Gas Chromatography for Analysis

Microcosms--

Soil- and sediment-water mixtures amended with synthetic organics were maintained as suspensions in 2-liter flasks by continuous stirring using a motor driven magnetic stirrer (Figure 6). To minimize abrasive wear, flexible polyvinyl chloride (Tygon) tubing was placed over the 2-inch (5.08 cm) teflon coated magnetic stirring bar. The 3-necked flasks were equipped with two platinum electrodes for monitoring redox potential, a combination electrode for measuring pH, a thermometer, a septum through which suspension samples could be obtained and acid or basic solutions could be added to adjust pH, separate inlet tubes for air and nitrogen, and an outlet tube that was connected to a water trap to prevent gaseous oxygen diffusion into the flask.

All suspensions were maintained at 28-30°C. Thin layers of insulating material were placed between the flask and the stirring motor as necessary to control heat transfer from the motor.

A saturated calomel reference electrode used with the platinum electrodes was connected to the suspensions with a saturated potassium chloride-agar salt bridge. The platinum electrodes were connected to a millivolt/pH meter (Beckman Zeromatic III or IV models) operated in the millivolt mode for monitoring and control of redox potential. A meter relay (General Electric Type 195 or 196) was connected to the recorder output of the millivolt meter. This meter relay switched on an aquarium air pump when the redox potential became more reducing than the selected redox level for each incubation flask. In the absence of oxygen, soil and sediment-water systems tend to become anaerobic or more reducing due to the activity of microbial populations. A low flow (1 to 4 ml/minute) of air during the air-pumping cycle slowly increased redox potential to the preset level at which time the meter relay would switch off the air pump. By regulating the addition of air to soil and sediment systems with appreciable microbial activity, oxidation-reduction levels can be controlled over a wide range.

Nitrogen gas was continuously purged through the suspension at a rate of about 5 ml/minute to: 1) flush excess oxygen from the suspensions at the end of an aeration cycle, 2) prevent an accumulation of

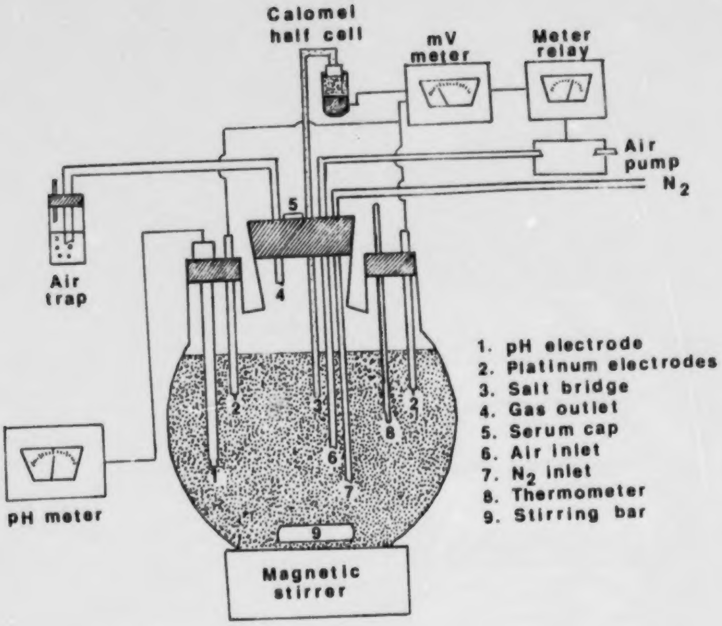
Calomel half cell
mV meter
Meter relay
Air pump
N$_2$
Air trap
pH meter
Magnetic stirrer
1
2
3
4
5
6
7
8
9
1. pH electrode
2. Platinum electrodes
3. Salt bridge
4. Gas outlet
5. Serum cap
6. Air inlet
7. N$_2$ inlet
8. Thermometer
9. Stirring bar

Figure 6. Laboratory microcosm for incubating soil and sediment suspensions under controlled pH and redox potential conditions.

gaseous decomposition products such as carbon dioxide or hydrogen sulfide that might affect microbial activity, and 3) remove air contamination should there be small leaks in the system.

The pH of the suspensions was checked daily and adjusted as necessary using a syringe to add a dilute solution of either hydrochloric acid or sodium hydroxide through the septum.

Each batch of soil or sediment material collected was uniformly mixed before 300 gram aliquots were added to incubation flasks. Fifteen hundred ml of water were added and stirring was initiated for the preincubation period. A preincubation period (prior to amending the sediment with a synthetic organic) was necessary to gradually achieve the desired pH and redox potential levels. Approximately 7 to 12 days were usually necessary to achieve the selected redox potential levels and this period was followed by another week at the desired pH and redox potential levels before the synthetic organics were added.

On sampling dates, a 50-ml glass syringe equipped with a glass needle was used to withdraw suspension aliquots from the incubation flasks. The samples were frozen immediately in 4 ounce (112 ml) glass jars fitted with aluminum foil-lined caps if they were to be stored before extraction.

Extraction Methods--

Methyl parathion--1. The samples were thawed if stored. 2. About 0.5 g sodium chloride was added to the thawed sediment-water mixture and then the sample was centrifuged for 15 minutes (IEC #266 or #277 rotor). 3. The supernatant solution was discarded (or poured into a separatory funnel if the solution phase was to be analyzed). 4. One to 2 ml of toluene was added, with mixing, to the wet sediment to inhibit microbial degradation during sample drying, then the sample was placed in a forced draft oven for drying at a temperature of 35-38°C. 5. When dry, the soil or sediment materials were finely ground and weighed into cellulose extraction thimbles. 6. The soil or sediment solids were extracted with 130 ml of acetone on a Soxhlet extraction apparatus for 4 hours. 7. The extracting solution was rinsed into a flask with acetone, then moisture was removed by filtering the solution through acetone-rinsed sodium sulfate. 8. The solution was then made to volume in 200 or 250 ml volumetrics with acetone. 9. The sample was concentrated if necessary.

2,4-D--1. The sample (1-2 g dried weight equivalent) was thawed, if stored. 2. Fifteen ml of 1 percent potassium hydroxide was added to the sample and the pH checked to confirm a pH of approximately 11 was achieved. 3. The samples were extracted by shaking with the alkaline solution for 15 minutes. 4. The alkaline extract was heated in a water bath at 45°C for 15 minutes, then centrifuged at 5000 rpm (Sorvall GS-3 rotor) for 30 minutes. 6. The supernatant was decanted through glass wool into a separatory funnel. 7. The potassium hydroxide extraction was repeated and the extracts combined in a separatory funnel. 8. The oven dry weight of the extracted soil or sediment material was determined. 9. Twenty ml of diethyl ether was added to the alkaline extract, the separatory funnel was shaken for 1 minute and the phases allowed to separate. 10. The potassium hydroxide phase (bottom layer) was transferred to a second separatory funnel and the ether layer discarded. 11. Steps 9 and 10 were repeated twice more. 12. The potassium hydroxide extract was transferred to another separatory funnel, and 1 ml (or more if necessary) of 9N sulfuric acid added to reduce the pH to 3. 13. Twenty ml of diethyl ether was added, the mixture shaken and the phases allowed to separate. 14. The ether layer was transferred to a flask. 15. Steps 13 and 14 were repeated and the ether extracts combined. 16. A pinch of acidified sodium sulfate was added to the combined ether extract and the ether evaporated to 5-10 ml under a stream of nitrogen. 17. The ether extract was then transferred to a 15 ml centrifuge tube and evaporated to dryness. 16. One ml of a fresh solution of diazomethane was added to each tube, the tube capped tightly, then heated for 15 minutes at 45°C in a water bath. 17. After methylation, one ml of hexane was added and the volume evaporated to 1 ml. 18. The methylated sample was then diluted to an appropriate concentration for GC analysis with hexane that had been dried by filtering through anhydrous sodium sulfate.

Aroclor 1254--1. The sample was thawed if stored. 2. About 0.5 grams of sodium chloride was added to the sediment-water mixture, then the sample was centrifuged for about 15 minutes to facilitate separation of the aqueous phase, and the clear supernatant was discarded. One ml of toluene was added to the sediment to retard microbial activity, then the sediment material was dried at 35-38°C in a forced draft oven. 4. The dried solids were finely ground and were transferred to tared cellulose thimbles and the sample weight determined. 5. The thimbles were placed in a Soxhlet extraction apparatus and extracted for 16 hours with a 40% hexane/60% acetone mixture. 6. The extract was transferred to a separatory funnel and the acetone removed by shaking with an addition of 100 ml of sodium chloride-saturated water. 7. This acetone removal step was repeated twice more with 50 ml of the sodium chloride saturated water. The Aroclor 1254 partitioned into the hexane was passed through anhydrous sodium sulfate to remove moisture and collected in a volumetric flask. The flasks were brought to volume with hexane.

Gas Chromatography--

For the degradation studies under controlled pH-redox potential conditions, all samples were analyzed by gas chromatography (Perkin-Elmer Model 3920B). A summary of the instrumental parameters is given in Table 1. Sample concentration was determined by comparing sample and standard peak areas, when an intergrator was used (Perkin-Elmer Model M-2), or by comparing sample peak height times the instrument attenuation with the peak height times instrument attenuation values of standards. For most methyl parathion and 2,4-D samples, the intergrator was used to record peak areas. For Aroclor 1254 which gives a multipeak chromatogram, five of the major characteristic peaks were identified, and the sum of peak height times attenuation for these peaks were compared for sample and standards to give sample concentration. The concentrations of samples were kept within the linear response range of the instrument, or dilutions were made as appropriate.

TABLE 1 . GAS CHROMATOGRAPHY PARAMETERS FOR METHYL PARATHION, 2,4-D, AND AROCLOR 1254

Parameter	Methyl Parathion	2,4-D	Aroclor 1254
Column	1.5% OV-17, 1.95% QF-1	3% OV-210	3% OV-1
Column dimensions	glass, 6' x ¼" O.D. (1.8 m x 6.35 mm O.D.)	glass, 6' x ¼" O.D. (1.8 m x 6.35 mm O.D.)	glass, 6' x ¼" O.D. (1.8 m x 6.35 mm O.D.)
Carrier gas	O-grade N_2	O-grade N_2	O-grade N_2
Carrier gas flow rate	70 ml/min	70 ml/min	70 ml/min
Injector temperature	230°C	230°C	230°C
Column temperature	200°C	170°C	190°C
Interface temperature	250°C	250°C	250°C
Detector	Nitrogen/Phosphorus specific (thermoionic)	ECD (275°C)	ECD (275°C)

Research and standard material for methyl parathion and 2,4-D were obtained from Chem Service, Inc. (West Chester, PA). The Aroclor 1254 was obtained from Applied Science (State College, PA). Identification and purity of the compounds from commercial sources were confirmed by comparisons of chromatograms with Analytical Reference Standards from the EPA Health Effects Research Laboratory.

Carbon Dioxide Analyses--

In selected degradation studies using the controlled pH-redox potential microcosms, carbon dioxide evolution from the microcosms was measured as an indication of microbial activity. The microcosms were operated in the usual manner, except that all air or nitrogen going into the suspensions passed through two sodium hydroxide traps connected in series to remove incoming carbon dioxide, and the exit gas stream was passed through another two alkaline traps (either 0.1 N or 0.2 N NaOH) to remove that carbon dioxide that was generated in the suspensions. Standardized acid and base solutions were used and the quantify of carbon dioxide trapped was measured by titrating the alkaline solution to determine the amount of base neutralized and then calculating the carbon dioxide equivalent.

Biometer Flasks Using Mineralization Rate of ^{14}C-Labeled Compounds for Analysis

Biometer flasks (Figure 7) were used for degradation studies in which collection of ^{14}C-labeled carbon dioxide was used to measure degradation of the compounds studied (Bartha and Pramer, 1965). Ten grams of soil or sediment material that had been air-dried and ground were weighed into flasks. To insure an active microbial population, all of the soil and sediment materials were inoculated after being weighed into flasks. The inoculate was prepared by obtaining a fresh sample of bayou water containing a small quantity of bottom sediment, mixing this well, and allowing the solids to settle. Then 0.5 ml of the supernatent was mixed with 100 ml of deionized water. Approximately 2 ml of this water (depending on the amount required to achieve field moisture capacity of each soil material) was added to the 10 grams of soil. A humidified nitrogen stream was continuously purged through those flasks designated for the reduced treatment, and similarly, air was used for those flasks designated for the oxidized treatment. Prior to adding the labeled compounds, the flasks were purged with air or nitrogen for 5 days to obtain reduced or oxidized conditions in the soil materials. Each experimental combination was replicated three times.

As the labeled compounds were mineralized to labeled carbon dioxide and purged from the biometer flasks, the labeled gas was collected in two sodium hydroxide traps connected in series to the outlet gas line from each flasks. One ml of the alkali trapping solution was transferred to 15 ml of a commercial liquid scintillation counting reagent in vials and the activity was measured on a Beckman liquid scintillation counter (Model LS100C). All compounds (methyl parathion, 2,4-D, and Aroclor 1254) were uniformly labeled in the aromatic ring.

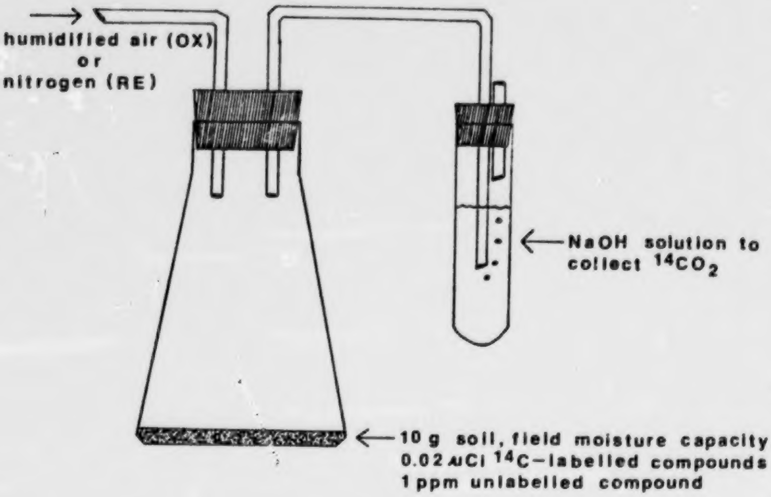
humidified air (OX)
or
nitrogen (RE)
NaOH solution to collect $^{14}CO_2$
10 g soil, field moisture capacity
0.02 µCi ^{14}C-labelled compounds
1 ppm unlabelled compound

Figure 7. Biometer flask used for degradation studies with ^{14}C-labeled compounds.

ADSORPTION STUDIES

Adsorption of Methyl Parathion and 2,4-D by 19 Soil and Sediment Materials

Soils--

To study the factors affecting pesticide adsorption, 19 soil and sediment materials were selected to include a broad range of physical and chemical properties. Samples were air-dried and ground to pass through a 2 mm sieve for characterization and adsorption studies.

Soil samples were characterized as previously described for pH, cation exchange capacity, organic carbon, particle size distribution, free iron oxides, and Ca, Al, and Mn extracted with the free iron oxides.

Pesticides--

The pesticides selected for this study were the insecticide methyl parathion (O-O-dimethyl-O-p-nitrophenyl phosphorothioate) and the herbicide, 2,4-D (2,4-dichlorophenoxyacetic acid). It would be expected that the partitioning of these pesticides between dissolved and adsorbed forms would be affected differently by changes in soil properties. The solubility of methyl parathion in water at 25°C is 50 ppm (Wauchope, 1978), and the solubility of 2,4-D in water is approximately 0.062% (Loos, 1969).

Pesticide standard compounds from Chem-Service, Inc. were amended with ^{14}C-labeled materials obtained from Pathfinder Laboratories, Inc. for this study. Stock solutions containing labeled methyl parathion and 2,4-D (specific activity 1 μCi/ml) were prepared in acetone and stored in the refrigerator. The stock solutions were diluted with water such that on a soil solids basis, the amended levels of compound and label were 1 μg compound/g and 0.1 μCi specific activity per g respectively. A batch equilibrium technique described below was used for this study (Leenher and Ahlriches, 1971).

Twenty milliliters of a given pesticide solution were added to 2 g of air-dried soil in a 50 ml stainless steel centrifuge tube, capped with teflon-lined lids and equilibrated for 2 hrs on a mechanical box shaker. Each soil treatment combination was replicated three times. Following equilibration, the tubes were centrifuged for 15 minutes at 12,000 rpm in a DuPont Sorvall SA-600 rotor. Aliquots of the clear supernatant solution (1 ml) were transferred to counting vials and ^{14}C-labeled material was measured on a Beckman Model LS100C liquid scintillation counter. To prepare a sample for counting, 1 ml of an aqueous sample was mixed with 15 ml of a commercial liquid scintillation counting reagent. Decreases in pesticide solution concentration were attributed to adsorption by the soil. After the 1 ml sample aliquot was removed at 2 hours, the caps were replaced on the centrifuge tubes and the equilibration continued for 22 more hours when another 1 ml aliquot was sampled. Thus data were obtained for 2-hour and 24-hour equilibrations. Each sample was counted for 10 minutes. Standards and blanks were also counted and included in calculations to get adsorption coefficients.

The amount of pesticides adsorbed on soils has been expressed as the soil-water distribution coefficient (K) calculated by the formula given below (Luchini et al., 1981; Wahid and Sethunathan, 1978).

$$K = \frac{\mu g \text{ adsorbed/g soil}}{\mu g \text{ dissolved/g solution}}$$

When the sorption of compounds is expressed as a function of the organic carbon content of a soil or sediment, a coefficient (K_{oc}) is generated that is dependent upon the organic component (Briggs, 1973; Hamaker and Thompson, 1972; Karickhoff et al., 1979; Khan et al., 1979).

$$K_{oc} = \frac{K}{\% \text{ OC}} \text{ (decimal equivalent)}$$

K_{oc} is equal to the distribution coefficient (K) divided by percent organic carbon in the respective soil or sediment. The K_{oc} value is a measure of the partitioning of the compound between an aqueous solution and a stationary organic phase (humus).

The Effect of pH and Redox Potential on the Adsorption of Methyl Parathion and 2,4-D

At the conclusion of selected degradation studies, an aliquot of the soil or sediment suspensions was removed, air-dried, and ground for adsorption studies on materials that had been incubated under controlled pH and redox potential conditions. The methods used were essentially the same as described in the preceding section.

The Effect of Redox Potential and Sample Processing Methods on the Adsorption of Pentachlorophenol

Collection of Research Material--

On October 9, 1980, sediment and water were collected from the area surrounding a 22 July 1980 ship collision on the Mississippi River Gulf Outlet near Shell Beach, Louisiana, where 25,000 pounds of granular PCP (pentachlorophenol) was spilled into the channel. Sediment samples were collected using a Peterson dredge. Water samples were collected by immersing 18.9 liter plastic carboys below the water surface and filling.

Adsorption-Desorption Study--

An adsorption-desorption study was conducted with PCP using Shell Beach sediment material preincubated as suspensions under reduced and oxidizing conditions by continuous purging with nitrogen or air, respectively. The pH of the reduced and oxidized suspensions was maintained at 6.8, the pH of the sediment as collected. A batch equilibrium adsorption technique was used (Leenher and Ahlriches, 1971) on 2 g-aliquots, oven-dry solids basis, of the wet sediment material. Based on the predetermined water:solids ratio, the solution volume of the sediment material was made up to a total of 20 mls with a ^{14}C-labelled PCP solution having a final activity of 3.5 x 10^{-4} µCi/ml in 50 ml stainless steel centrifuge tubes. Other sample aliquots were dried and ground after the incubation under oxidized and reduced conditions to determine the effect of this sample processing step on adsorption and desorption of PCP. Concentrations of unlabelled PCP in the added solution was 1 µg ml^{-1}. The tubes were sealed with teflon-lined stainless steel caps and the sediment-solution mixture equilibrated for 2 hrs on a reciprocating box shaker. Following this equilibration, the tubes were centrifuged for 15 minutes at 12,000 rpm (Sowall SA-600 rotor) and a 1 ml-aliquot of the clear supernatent solution transferred to an LS vial for ^{14}C assay by liquid scintillation counting. The ^{14}C-labelled sediment aliquots were then resealed, the equilibration continued by shaking for an additional 22 hours, and a 1 ml aliquot removed for ^{14}C counting as described previously. For the desorption phase, the supernatant after the 24-hr equilibration was discarded and the sediment material was dried at low temperature, then finely ground within the tube. Twenty ml of deionized water was added, the suspension equilibrated for 2 hrs by shaking, and a solution aliquot taken for ^{14}C counting as done for the adsorption phase. The adsorption-desorption studies were done using triplicate subsamples.

The amount of PCP adsorbed or desorbed was expressed as the solid phase:aqueous phase distribution coefficient (K) calculated by the formula (Luchini et al., 1981):

$$K = \frac{\mu g \text{ adsorbed/g soil}}{\mu g \text{ dissolved/g solution}}$$

SECTION 3

RESULTS AND DISCUSSION

PROPERTIES OF SOIL AND SEDIMENT MATERIALS STUDIED

Selected physical and chemical properties of the soil and sediment materials studied in this project are given in Table 2. Materials number 1, 2, 3, 4, 10, 12, 13, 17, and 20 are sediments. The remainder are identified by a soil series name and are topsoils (A or Ap horizons) except for number 5 which is a subsoil or B horizon material.

CONCENTRATION EFFECTS OF METHYL PARATHION AND 2,4-D ON THE RATE OF SOIL REDUCTION

When an oxidized soil is flooded such that oxygen transport is greatly restricted, soils with appreciable microbial activity become more reducing as indicated by a decrease in redox potential.

In the Crowley soil material amended with varying levels of 2,4-D, redox potential for all treatments decreased from about 450 to 500 mv (indicating moderately oxidizing conditions) to 0 to 50 mv in six days with no clear indication that 2,4-D levels affected reduction (Figure 8). Except for approximately 18 days being required to reach minimum Eh levels in the Cecil soil material, the results were similar with this soil in that levels of 2,4-D did not appear to affect the rate of reduction (Figure 9).

Methyl parathion amendments did apparently affect the rate of decrease in redox potential in both soils (Figures 10 and 11). Redox potential levels in control soil materials were generally much lower than in the amended materials during the phase of the incubations when the soils were gradually becoming more reduced. At the concentrations included in these particular soil materials, the data suggest methyl parathion may stress microbial populations more than 2,4-D even at levels below 100 ppm.

Although a change in redox potential is certainly a primary indication of microbial activity, other important changes also occur as a soil becomes more reduced. The pH of acid soils tends to increase toward neutrality when subjected to flooding that results in development of anaerobiosis (Patrick and Mikkelsen, 1971). An increase in pH with time and decreasing redox potential was observed for all combinations of soils, compounds, and concentrations. In the Crowley soil amended with 2,4-D, pH increased more rapidly in the control than the amended soil material and remained higher (especially when compared to the 75 ppm treatment) during the first 25 days, but there was considerable switching of relative pH levels of the various treatments over the next 25 days indicating considerable experimental variability within the narrow pH range of the samples (Figure 12). There was also no indication of 2,4-D concentration effects in the Cecil soil (Figure 13). In contrast, methyl parathion did appear to retard the rate of increase in pH as both

TABLE 2. SELECTED PHYSICOCHEMICAL PROPERTIES OF SOIL AND SEDIMENT MATERIALS

				Organic	Particle size distribution			Ammonium oxalate extractable			
	Soil material	pH	CEC	matter	Sand	Silt	Clay	Fe	Al	Ca	Mn
			meq/100 g soil	-- % --	-----------	%	-----------	------------	μg/g	----------	
1.	Airplane Lake[1]	6.8	23.50	6.53	36.2	52.6	11.2	4090	2110	36	16
2.	Atchafalaya River[1]	7.6	1.00	0.42	91.8	1.7	6.5	2565	422	19	126
3.	Bayou Chevreuil[1]	5.4	41.00	5.92	21.3	36.6	42.1	8190	2032	42	253
4.	Calcasieu River[1]	7.0	20.50	3.95	27.1	45.0	27.9	4720	1553	30	200
5.	Cecil Subsoil	5.6	9.00	0.74	21.3	6.8	71.9	8165	2560	92	36
6.	Cecil Top Soil	5.1	5.50	2.88	40.0	30.0	30.0	1980	1755	2	126
7.	Chastain	3.4	39.00	5.14	33.8	23.2	43.0	14100	3380	45	61
8.	Crowley	6.4	8.88	3.71	33.2	55.6	11.2	9100	2220	18	499
9.	Gallion	6.8	4.00	0.87	73.7	19.0	7.3	1155	512	29	91
10.	Hartwell Lake[1]	5.3	13.50	3.29	17.5	39.0	43.5	37750	4965	122	786
11.	Lafitte Muck	4.0	57.00	26.58	56.5	15.3	28.2	10100	3120	43	43
12.	Lake Pontchartrain[1]	3.4	2.00	0.94	94.2	2.1	3.7	699	238	63	40
13.	Lake Providence[1]	7.4	21.00	2.63	53.1	45.0	1.9	16550	1725	88	565
14.	Leeville	7.1	11.50	3.47	65.7	13.8	20.5	2940	1387	23	90
15.	Loring	4.3	32.00	9.92	46.9	36.2	16.9	23800	2800	65	502
16.	Mhoon	7.0	6.00	0.93	74.7	16.0	9.3	1758	589	29	144
17.	Mississippi River[1]	6.8	16.00	1.99	27.8	59.7	12.5	9140	2030	180	559
18.	Norwood	7.8	4.50	0.97	76.2	17.1	6.7	355	273	26	76
19.	Shubuta	3.9	1.50	0.75	87.0	4.4	8.6	298	354	40	110
20.	Barataria Bay[1]	7.3	19.20	5.17	39.0	33.0	28.0	≅4000	N.A.[2]	N.A.[2]	N.A.[2]

---

[1] Sediment

[2] Not available

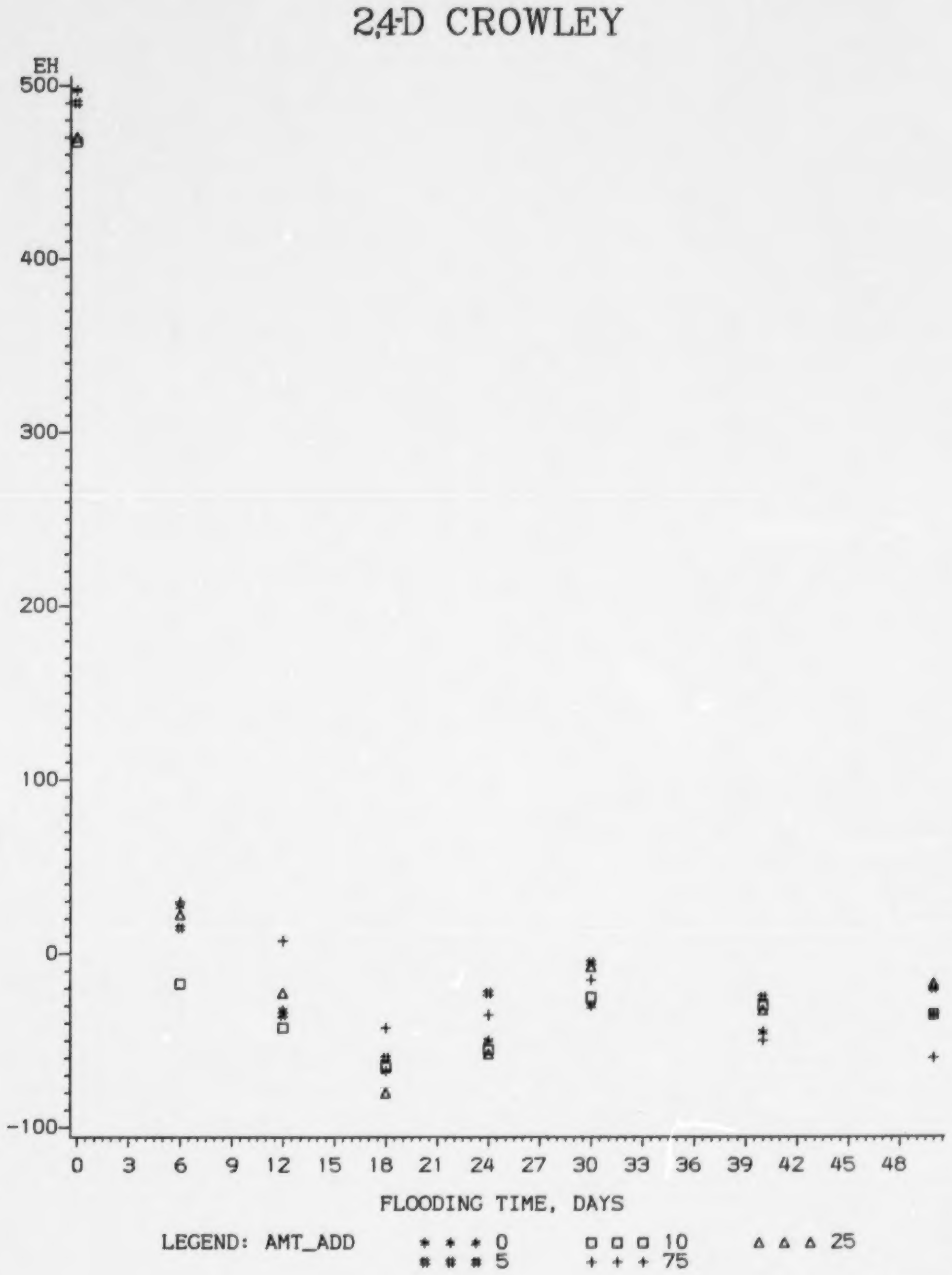

Figure 8. Redox potential levels (Eh) with time in a Crowley soil material amended with varying concentrations of 2,4-D and subjected to flooding.

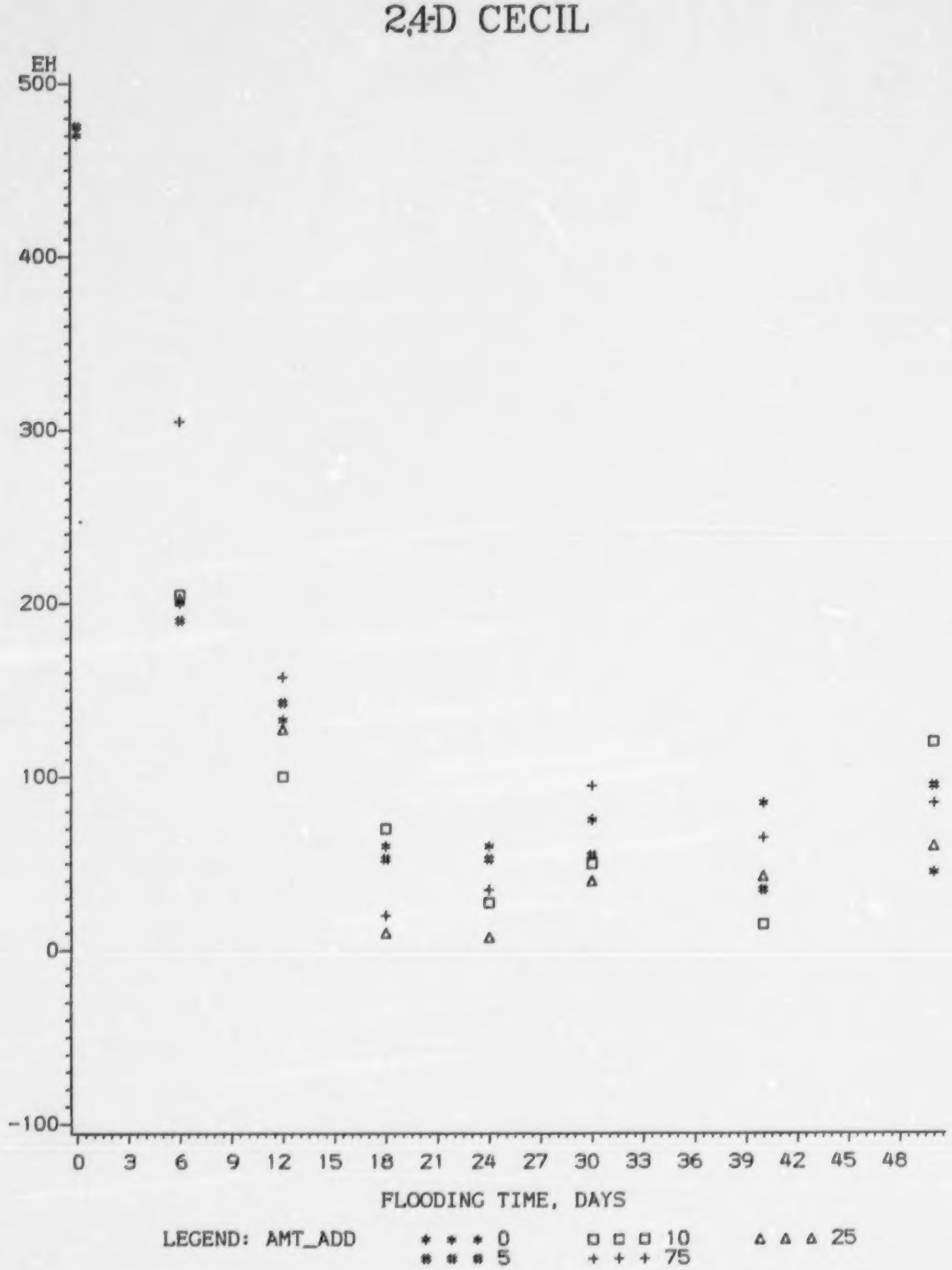

Figure 9. Redox potential levels (Eh) with time in a Cecil soil material amended with varying concentrations of 2,4-D and subjected to flooding.

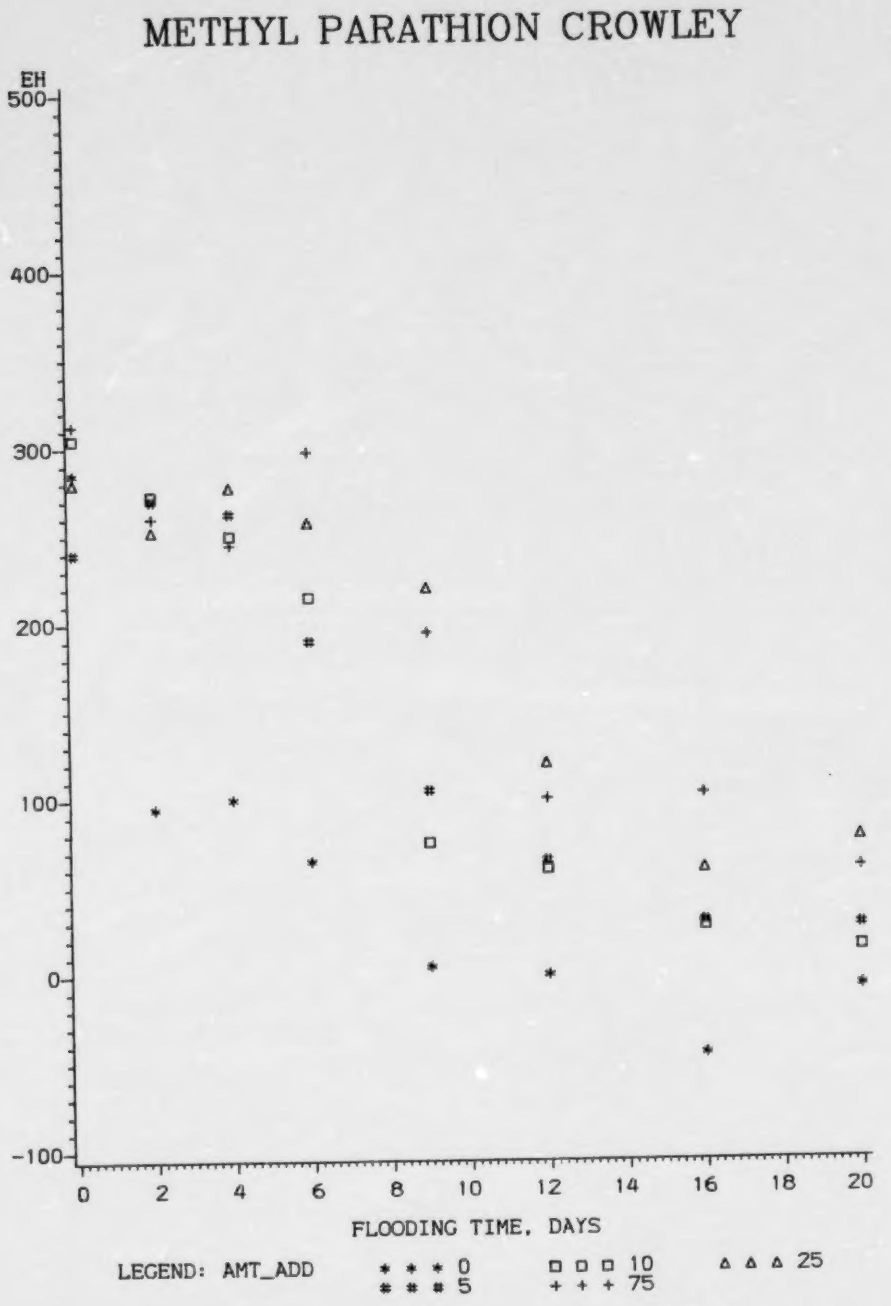

Figure 10. Redox potential levels (Eh) with time in a Crowley soil material amended with varying concentrations of methyl parathion and subjected to flooding.

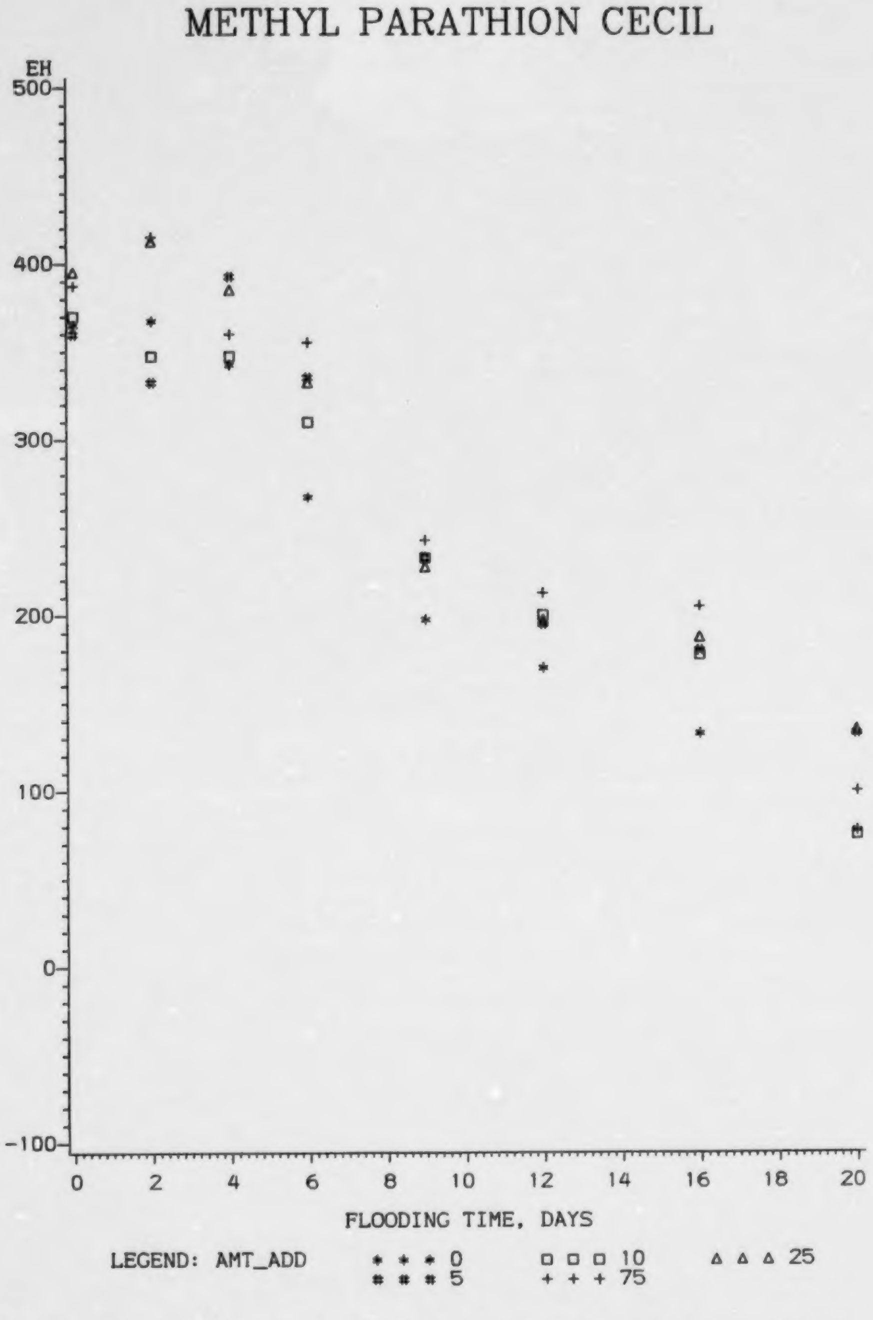

Figure 11. Redox potential levels (Eh) with time in a Cecil soil material amended with varying concentrations of methyl parathion and subjected to flooding.

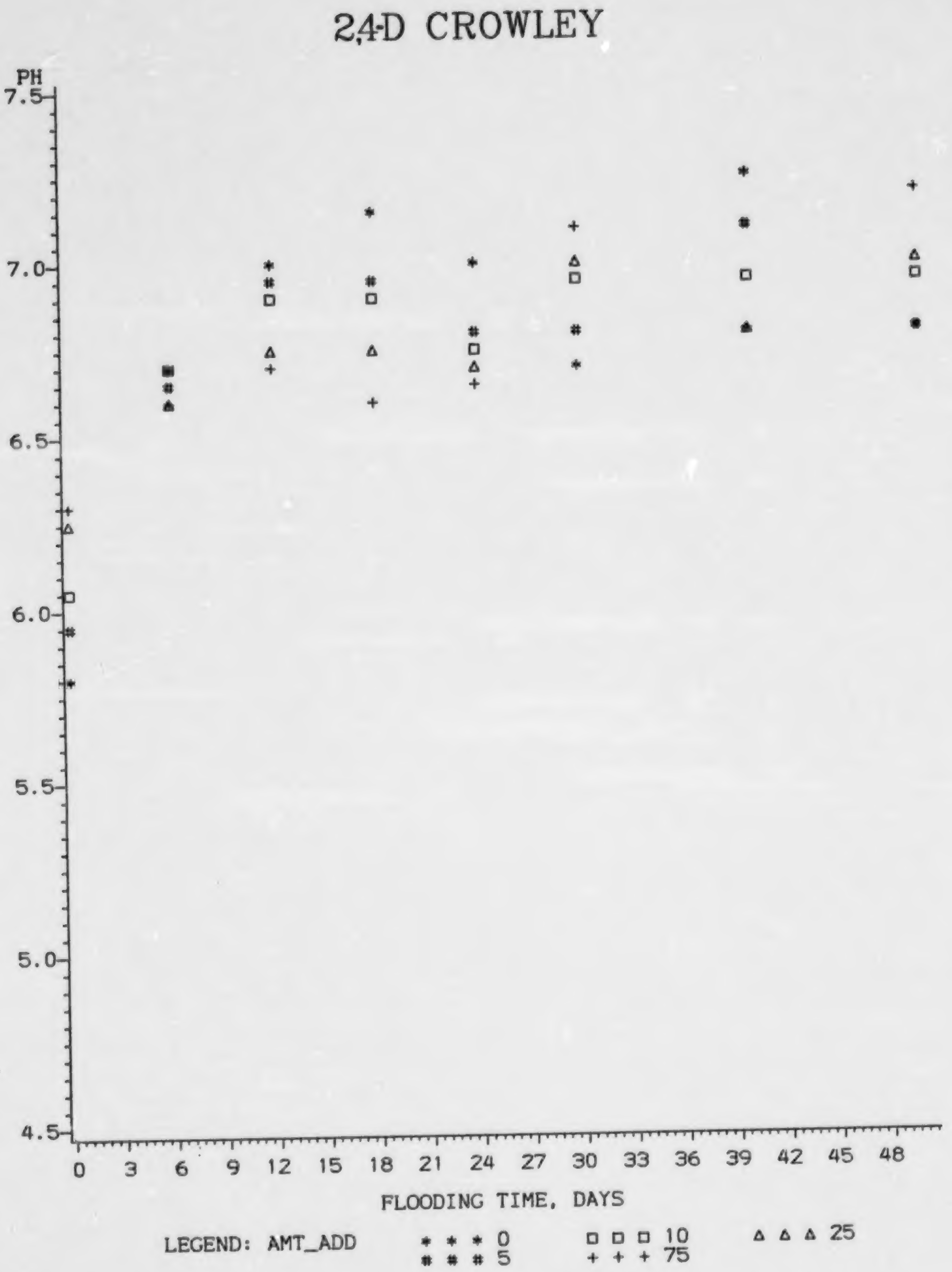

Figure 12. pH values with time in a Crowley soil material amended with varying concentrations of 2,4-D and subjected to flooding.

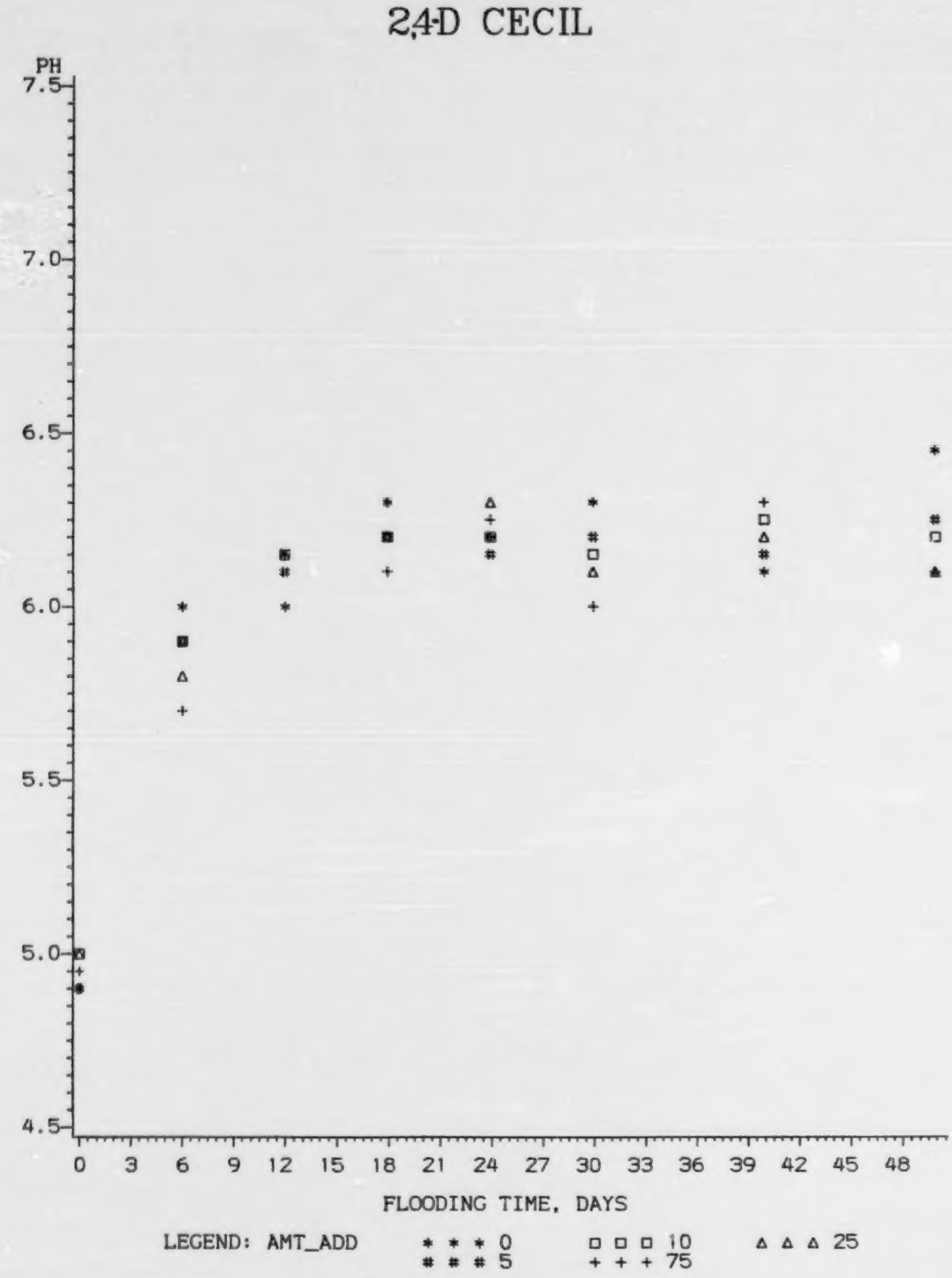

Figure 13. pH values with time in a Cecil soil material amended with varying concentrations of 2,4-D and subjected to flooding.

soils became more reducing (Figures 14 and 15). In the Crowley soil, the pH at 0 ppm was consistently above all other treatment levels and about 0.5 pH units above the 75 ppm treatment. This was also true of the changes in pH in the methyl parathion treated Cecil soil, although in both soils, there was considerable variability in relative pH levels at the intermediate concentrations.

The levels of soluble and exchangeable Fe and Mn are substantially affected by changes in pH and redox potential in many soils and sediments (Gotoh and Patrick, 1972; Gotoh and Patrick, 1974; Gambrell et al., 1977). Both tend to be more mobile or available with decreasing redox potential and pH. Flooding the Crowley and Cecil soils resulted in a reduction in redox potential and an increase in pH. Thus the separate influence of pH and redox potential changes in these two soils would tend to have opposite effects on mobilization of Fe and Mn such that considerable variability in Fe and Mn levels might be expected. All treatment combinations gave less than 3 ppm of soluble plus exchangeable Fe at time zero, but after that, there was substantial variability in Fe levels, both with time and concentration (Tables 3 and 4). However, the methyl parathion controls (0 ppm) consistently had higher levels of mobile Fe than materials that were amended with methyl parathion during the early part of the experiment before substantial degradation may have occurred. An examination of these Eh, pH, and Fe levels with time suggest that the changes in redox potential in these soils may have influenced Fe mobility more than the changes in pH that occurred.

In the Crowley and Cecil soil materials amended with 2,4-D, soil reduction did substantially increase soluble plus exchangeable Mn levels, though no 2,4-D concentration effects were apparent (Tables 3 and 4). In the methyl parathion-amended soil materials, the soluble plus exchangeable Mn levels were consistently greater in the controls, probably reflecting the more rapid rate of reduction in soils receiving no methyl parathion.

Zinc of course is an essential plant nutrient that is not subject to valence charge changes as a consequence of changing soil pH or redox potential conditions. However, the readily available concentrations of zinc are affected by both pH and redox potential conditions. In flooded soils and sediments, it is known that increasing pH and decreasing redox potential tend to decrease levels of soluble and exchangeable zinc (Gambrell et al., 1977; Jugsujinda, 1975).

Zinc levels tended to decrease slightly with time for all combinations of soil materials and compounds, but there were no apparent pesticide concentration effects over the narrow range of change in zinc concentrations observed (Tables 3 and 4). A decrease in readily available soil zinc levels would be expected both from the increase in soil pH and the decrease in redox potential observed with time when these soil materials were flooded.

Table 5 indicates the association (R^2 values) between water soluble plus exchangeable levels of Fe, Mn, and Zn with pH and redox potential changes that occurred upon flooding the Crowley and Cecil soil materials.

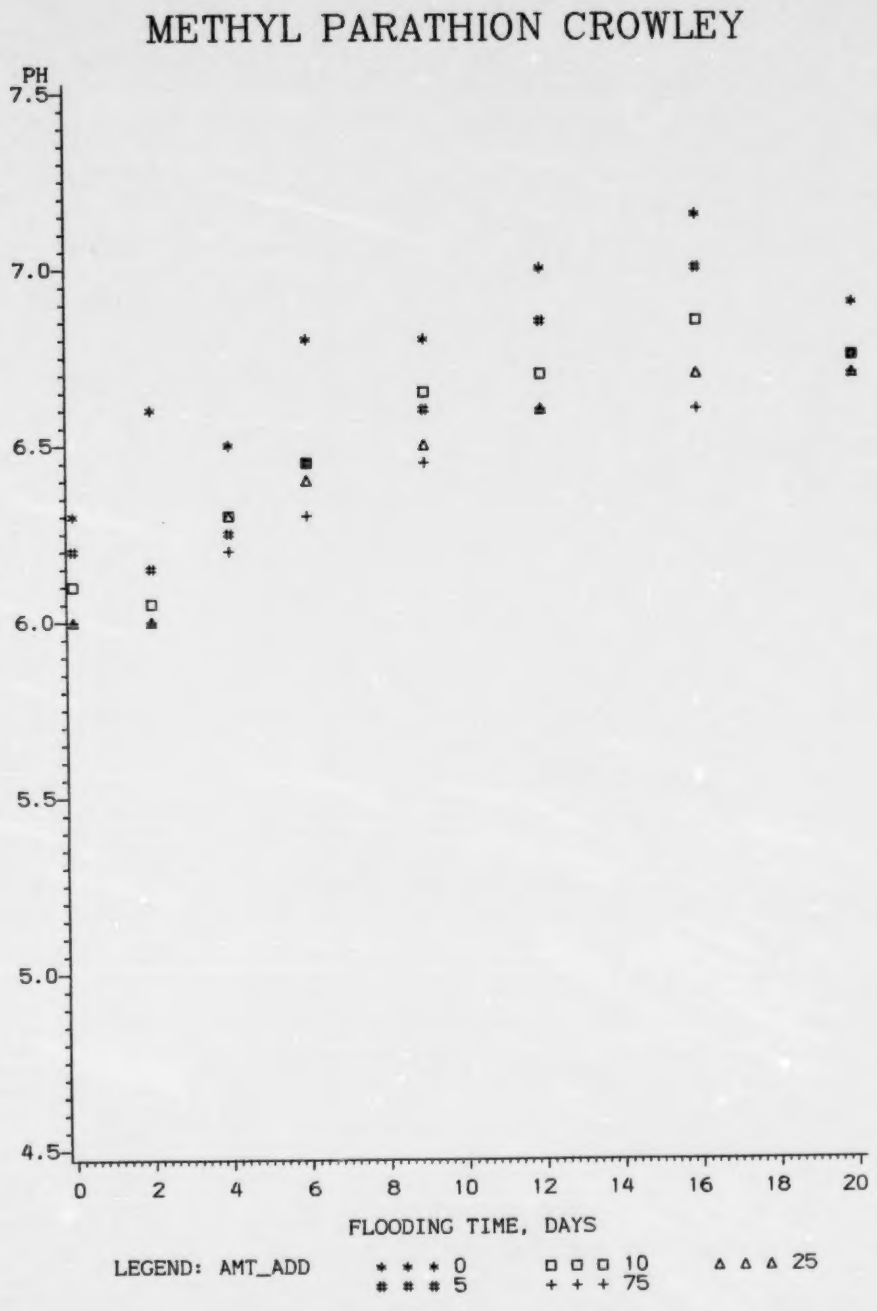

Figure 14. pH values with time in a Crowley soil material amended with varying concentrations of methyl parathion and subjected to flooding.

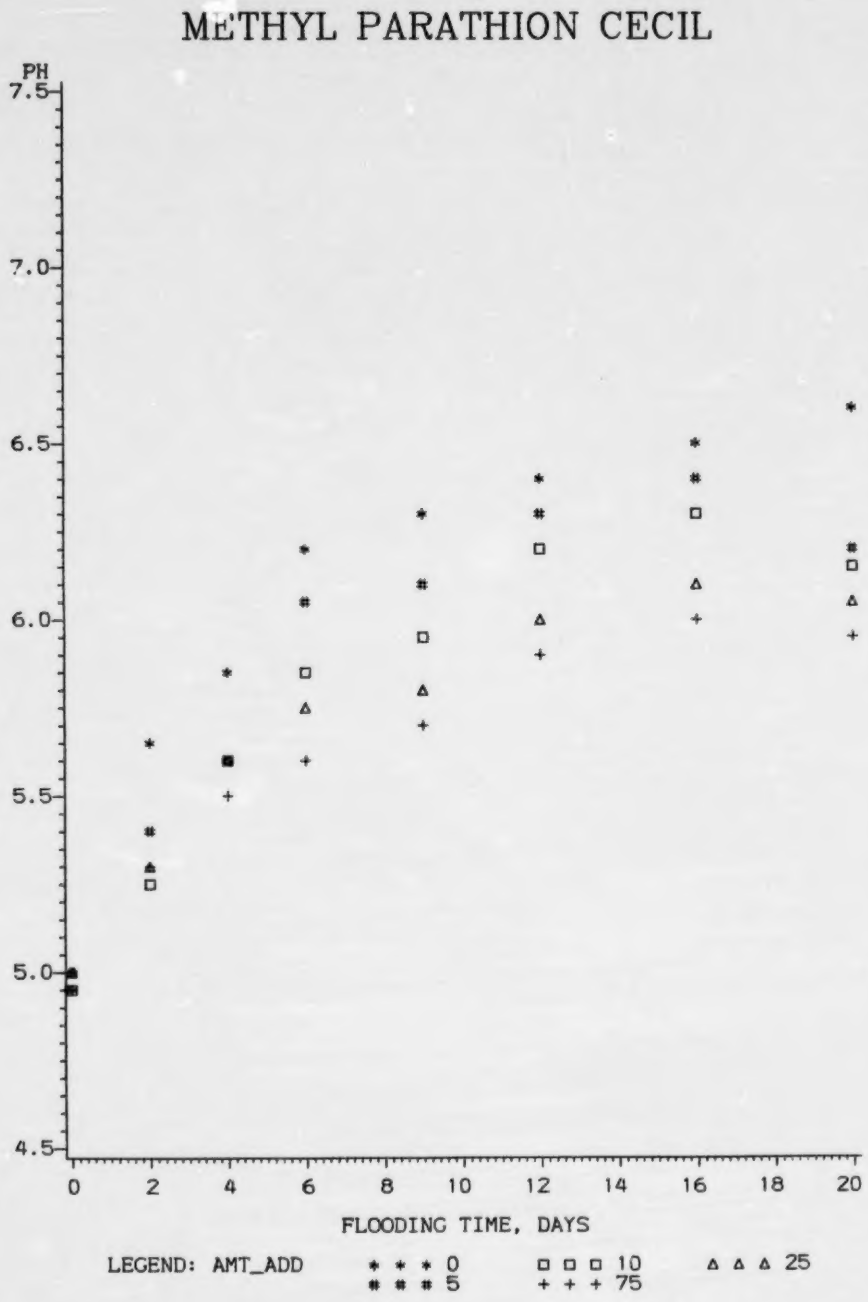

Figure 15. pH values with time in a Cecil soil material amended with varying concentrations of methyl parathion and subjected to flooding.

TABLE 3. SOLUBLE PLUS EXCHANGEABLE FE, MN, AND ZN LEVELS ON SELECTED SAMPLING DATES IN TWO SOILS AMENDED WITH VARYING CONCENTRATIONS OF METHYL PARATHION[1]

Soil material	Incubation time, days	Concentration added	Soluble + exchangeable		
			Fe	Mn	Zn
		ppm	ppm	ppm	ppm
Crowley	2	0	5.5	161	2.8
	2	10	.3	33	2.5
	2	75	.3	27	2.3
	9	0	129	204	2.4
	9	10	21	153	1.1
	9	75	1.1	107	2.4
	16	0	99	144	1.4
	16	10	36	126	1.8
	16	75	2.1	102	0.7
Cecil	2	0	2.9	3.6	2.3
	2	10	2.0	2.6	2.2
	2	75	1.7	3.6	2.3
	9	0	3.2	31.5	2.2
	9	10	0.7	25.8	1.7
	9	75	2.2	29.8	0.8
	16	0	12.0	45.2	2.0
	16	10	5.0	38.7	0.7
	16	75	1.5	38.6	1.3

[1] Mean value of two replicates.

TABLE 4. SOLUBLE PLUS EXCHANGEABLE FE, MN, AND ZN LEVELS ON SELECTED SAMPLING DATES IN TWO SOILS AMENDED WITH VARYING CONCENTRATIONS OF 2,4-D[1]

Soil material	Incubation time, days	Concentration added	Soluble + exchangeable Fe	Mn	Zn
		ppm			
Crowley	6	0	1.8	330	1.1
	6	10	1.9	322	2.3
	6	75	1.4	325	1.4
	24	0	20.7	340	1.4
	24	10	18.1	372	1.1
	24	75	18.0	364	1.3
	40	0	6.3	144	0.8
	40	10	5.2	292	0.6
	40	75	19.7	275	1.0
Cecil	6	0	3.2	44	2.6
	6	10	2.4	47	2.7
	6	75	0.5	42	2.9
	24	0	2.2	50	2.6
	24	10	3.4	50	3.0
	24	75	2.6	50	3.1
	40	0	13.7	54	1.6
	40	10	14.7	50	1.4
	40	75	5.6	51	1.6

[1] Mean value of two replicates.

TABLE 5. R^2 VALUES FOR FE, MN, AND ZN AS INFLUENCED BY SOIL PH AND REDOX POTENTIAL

Dependent variable	Independent variable	Crowley, 2,4-D	Cecil, 2,4-D	Crowley, methyl parathion	Cecil, methyl parathion
		----------	---------- R^2	----------	----------
Fe	redox potential	.23**	.08*	.32**	.36**
	pH	.27**	.10**	.30**	.37**
Mn	redox potential	.80**	.79**	.57**	.81**
	pH	.44**	.84**	.55**	.66**
Zn	redox potential	.04	.09*	.02	.06*
	pH	.10**	.09*	.02	.13**
		80 obs[1]	78 obs	79 obs	80 obs

---

*R^2 values followed by a single asterisk are significant at the 5% level.

**R^2 values followed by a pair of asterisks are significant at the 1% level.

[1] Number of observations.

There was not a good relationship between Fe or Zn levels and the physicochemical parameters of pH and redox potential (though many of the Fe associations were statistically significant). All of the Mn levels were significantly associated with pH and redox potential conditions and most of the R^2 values were high.

DEGRADATION STUDIES

Controlled pH-Redox Potential Microcosms

Degradation as Indicated by a Decrease in Recovery of Parent Compound vs. Time --

The laboratory microcosms using stirred suspensions offer the advantage of precise control of selected soil and sediment physicochemical conditions as well as the maintenance of uniform conditions throughout the material being studied. As discussed elsewhere, the relative treatment effects on degradation observed with these systems provide useful information that cannot be obtained by other experimental techniques, but the rate of degradation observed may not be applicable to in situ degradation rates.

For the controlled pH/redox potential experiments, the data were plotted as the log of concentration, in µg/g, vs. time in days. Log plots of concentration (or percent of compound remaining) vs. time are frequently used to illustrate degradation rates in the literature (Paris et al., 1982; Liu et al., 1981; Wolfe et al., 1977; Perdue and Wolfe, 1982). First order degradation kinetics are indicated if these plots result in straight lines. Correlation coefficients are often given to indicate how well the data points fit a straight line. In the controlled pH/redox potential studies, we have presented the data as the log of concentration vs. time and have also included correlation coefficients.

Methyl parathion--The degradation of methyl parathion under controlled pH and redox potential conditions has been studied in five soil or sediment materials (Figures 16-24). Figures 16 and 17 indicate the decrease in recovery of methyl parathion in sediment and water phases respectively of a Calcasieu River sediment material incubated at pH 8.0. It is readily apparent that redox potential substantially affects the rate of degradation of methyl parathion in this experiment as recovery had decreased to essentially zero after four days at -150 mv. However, it is also apparent that under the imposed experimental conditions, methyl parathion rapidly degrades under oxidizing conditions as well. While levels decreased to about 1 percent of spiking levels in 2 days at -150 mv (strongly reducing conditions), 6 days were required to get down to about 10% of spiking levels at 450 mv (oxidized conditions). Changes in levels of methyl parathion in the aqueous phase generally correspond to changes in the sediment phase.

Figures 18 and 19 give the change in recovery of methyl parathion with time in Barataria Bay sediment-water suspensions incubated at pH 7 and 5 respectively. At pH 7, the rate of degradation as indicated by compound recovery was much the same as found for the Calcasieu River

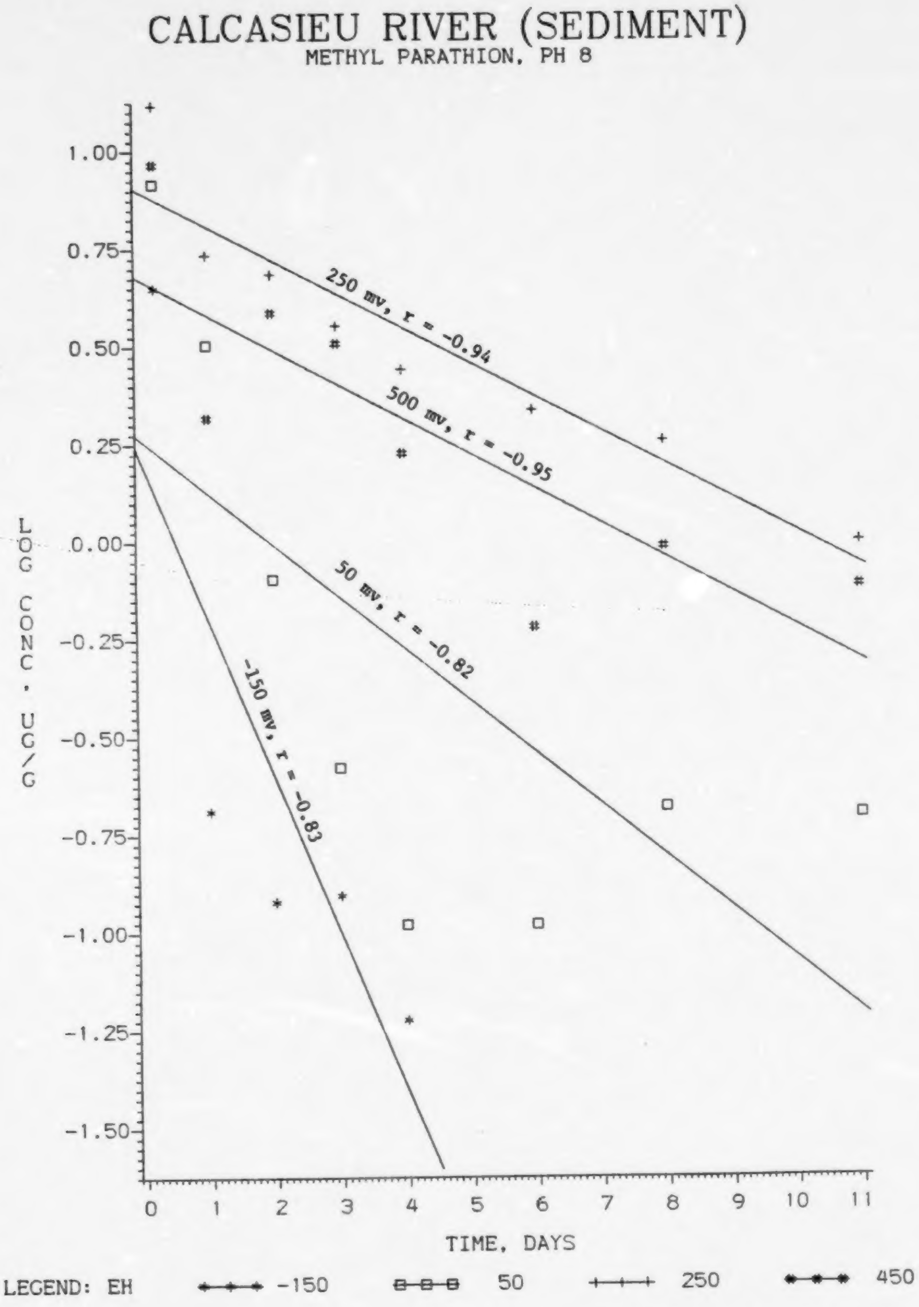

Figure 16. The effect of redox potential on the recovery of methyl parathion from a Calcasieu River sediment material incubated at pH 8.

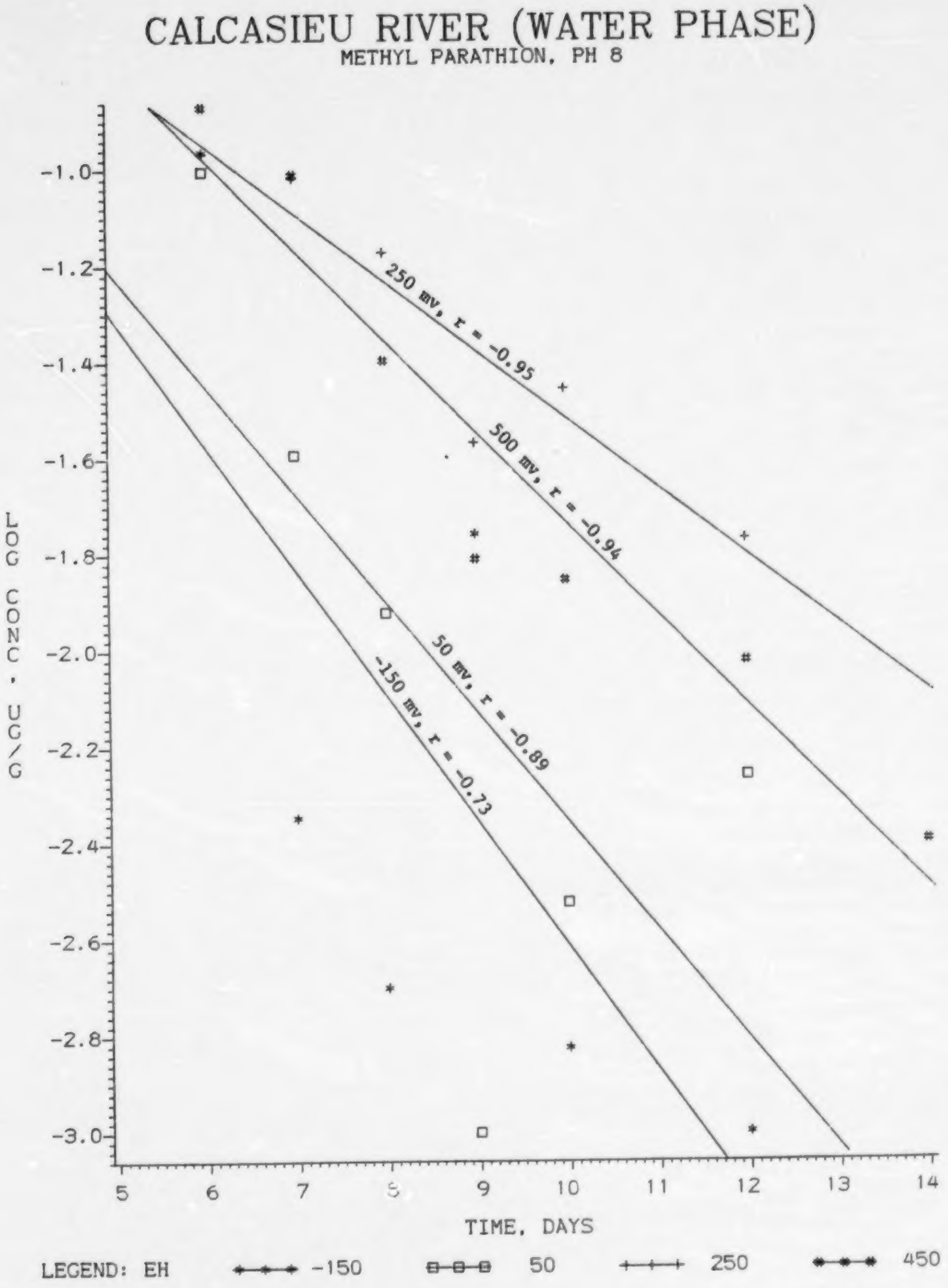

Figure 17. The effect of redox potential on the recovery of methyl parathion from the aqueous phase of a Calcasieu River sediment suspension incubated at pH 8.

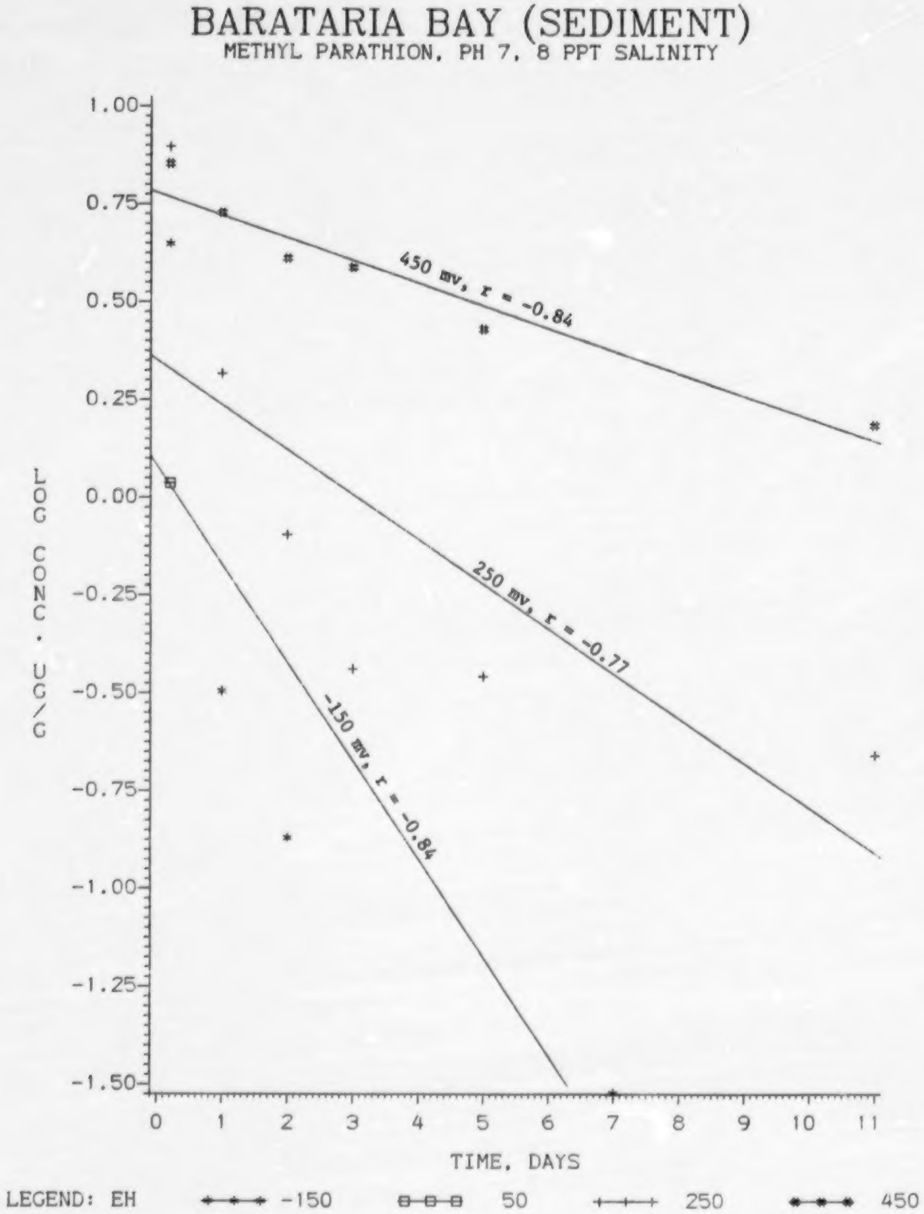

Figure 18. The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 7 and 8 ppt salinity.

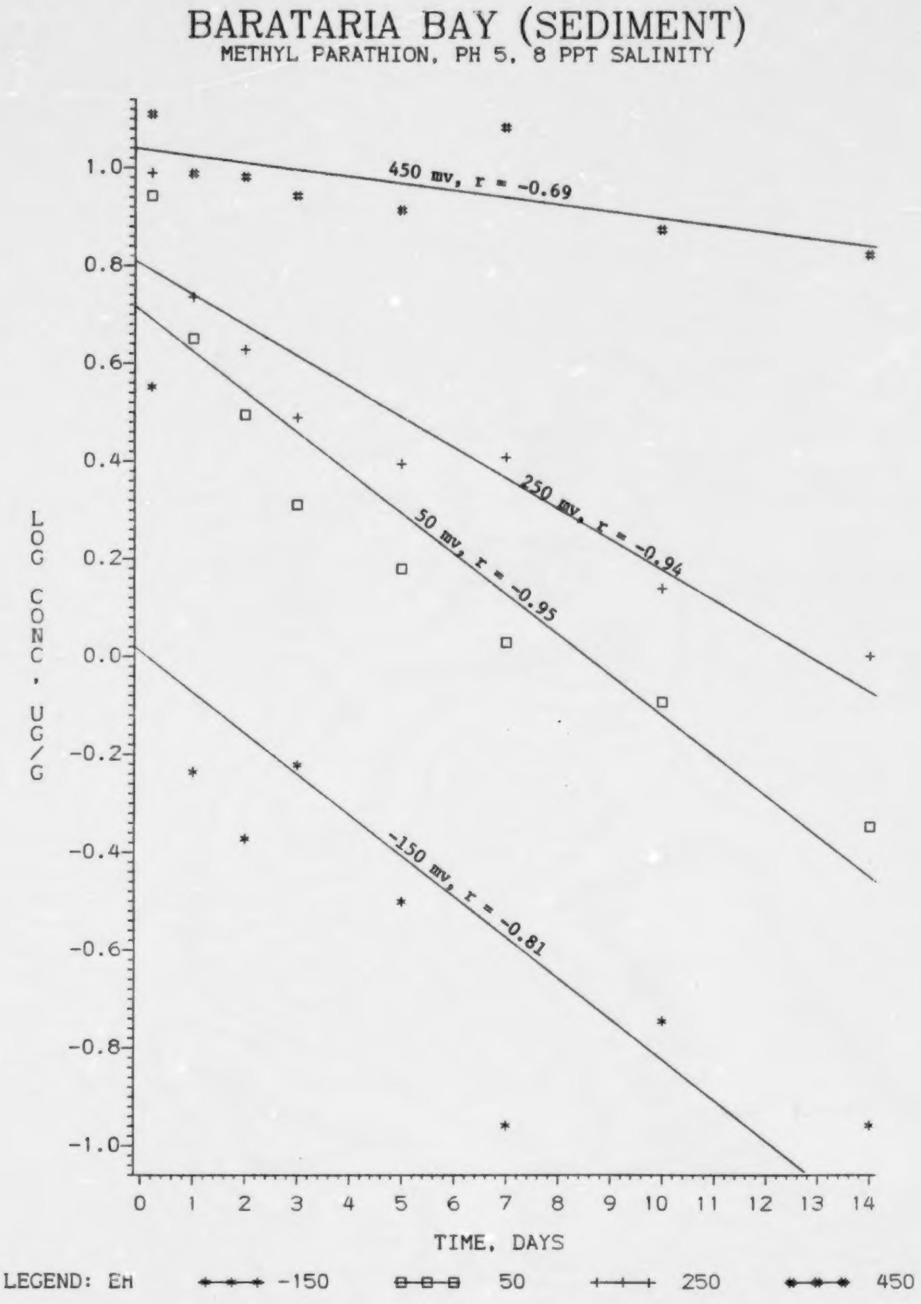

Figure 19. The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 5 and 8 ppt salinity.

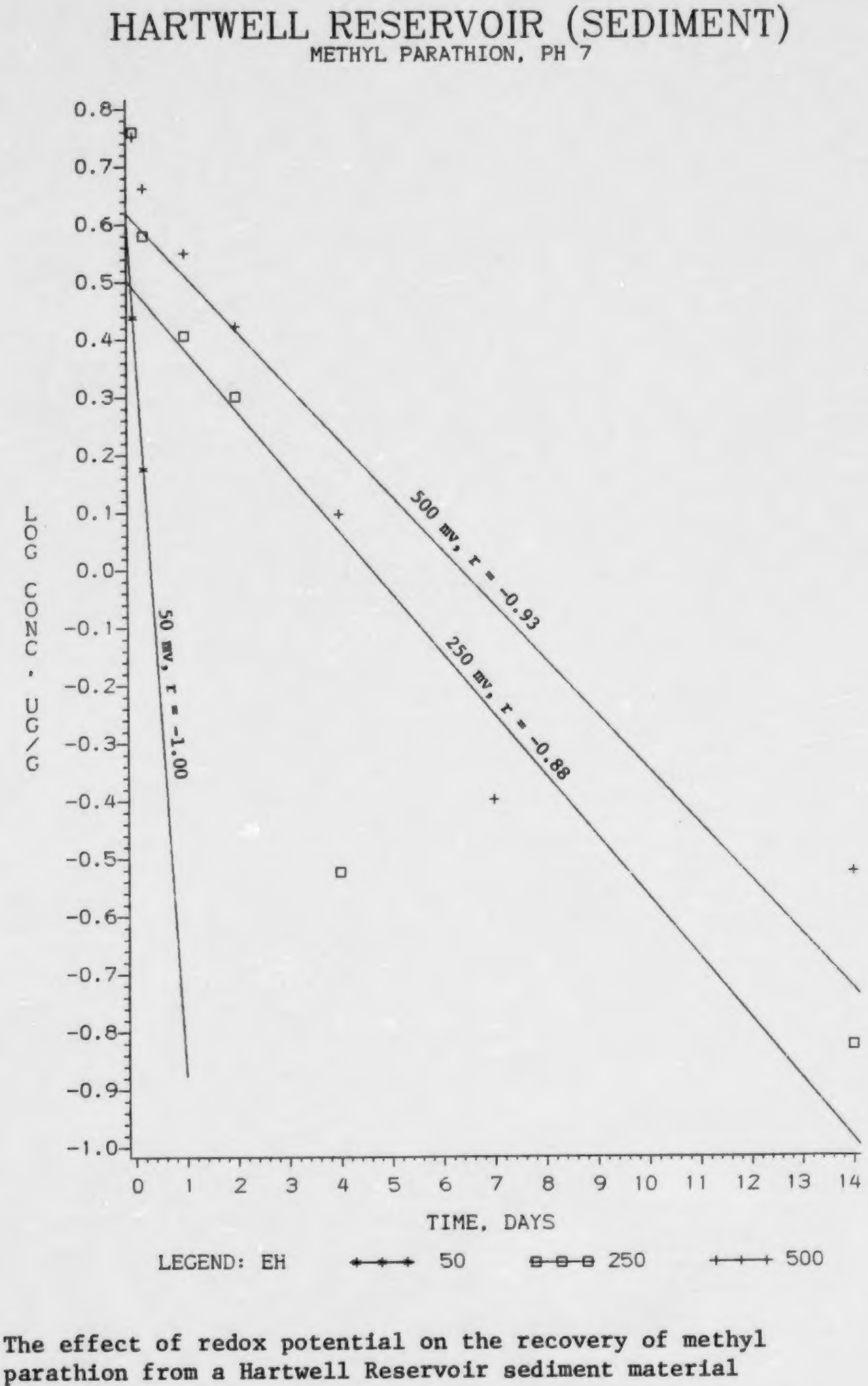

Figure 20. The effect of redox potential on the recovery of methyl parathion from a Hartwell Reservoir sediment material incubated at pH 7.

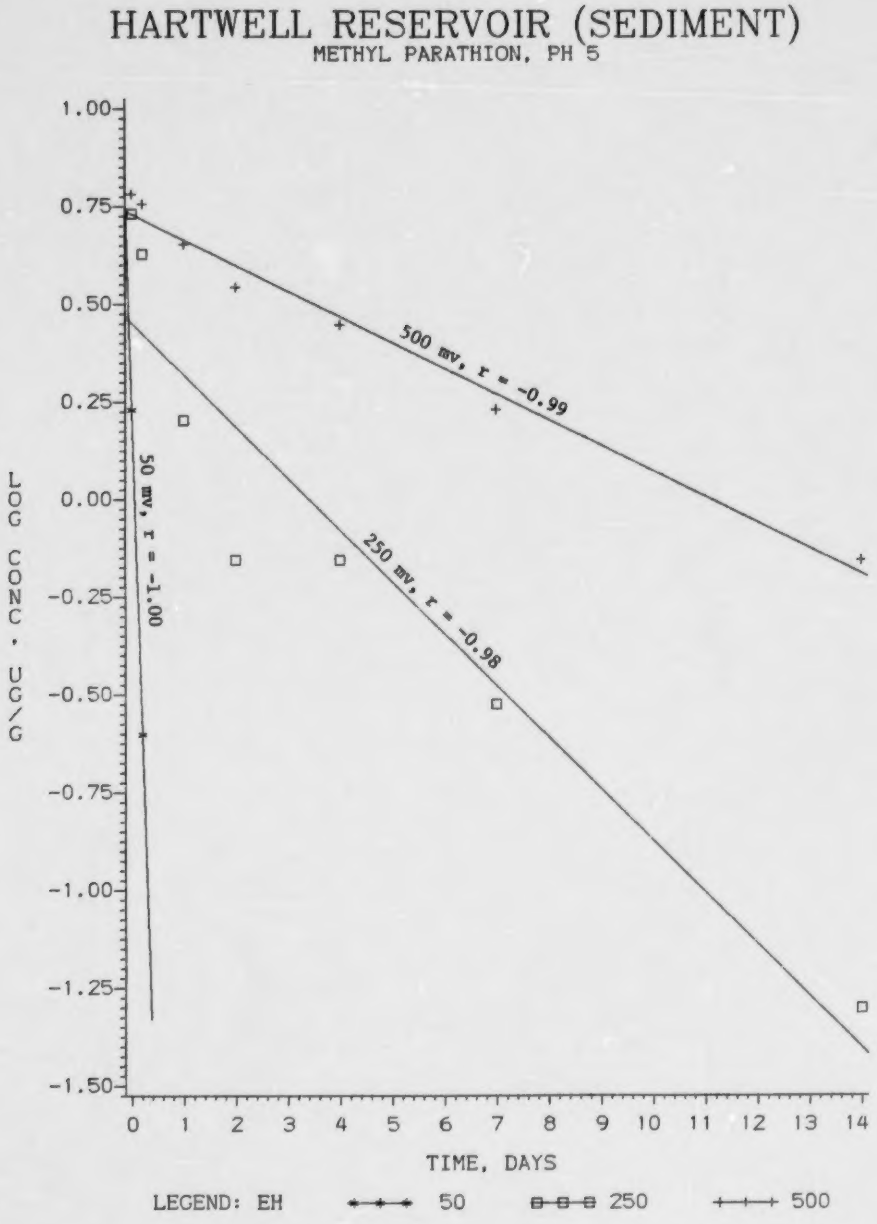

Figure 21. The effect of redox potential on the recovery of methyl parathion from a Hartwell Reservoir sediment material incubated at pH 5.

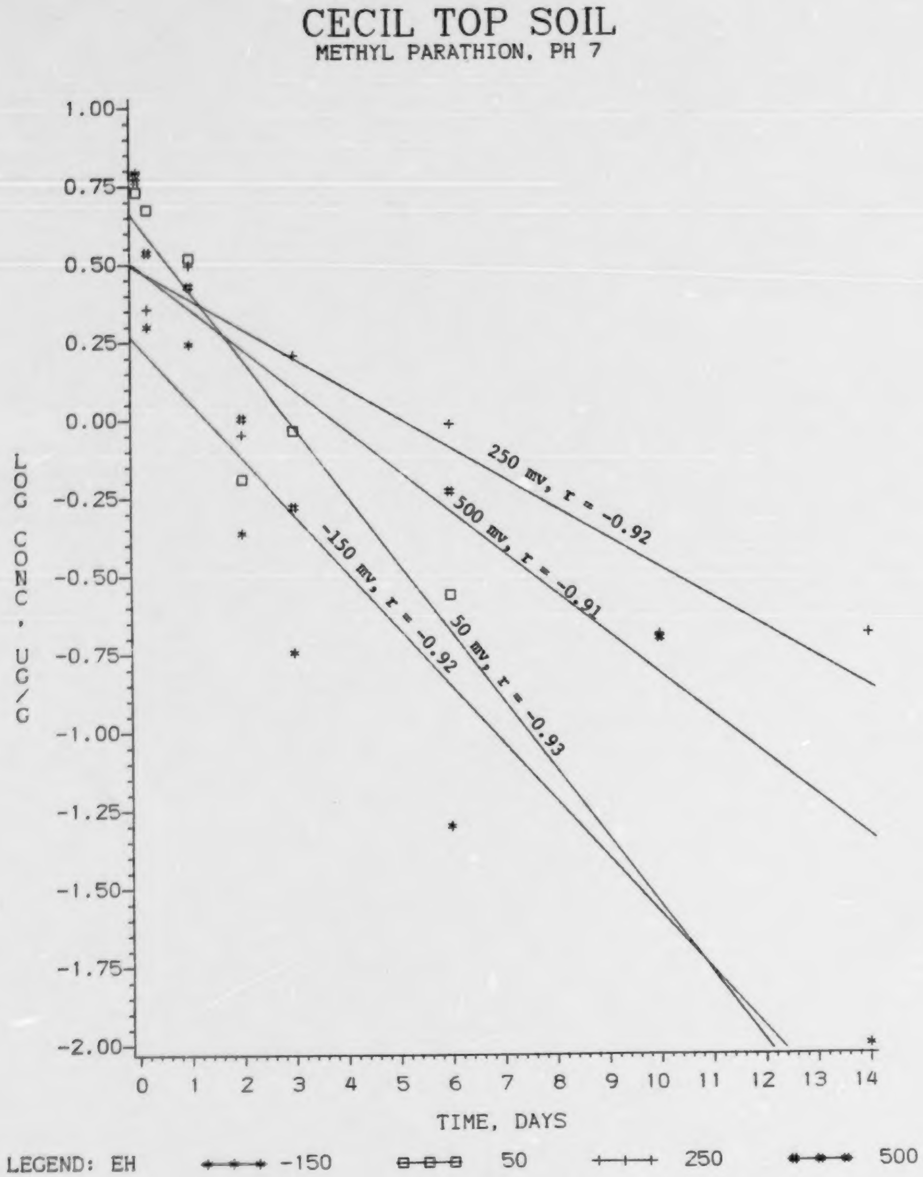

Figure 22. The effect of redox potential on the recovery of methyl parathion from a Cecil topsoil material incubated at pH 7.

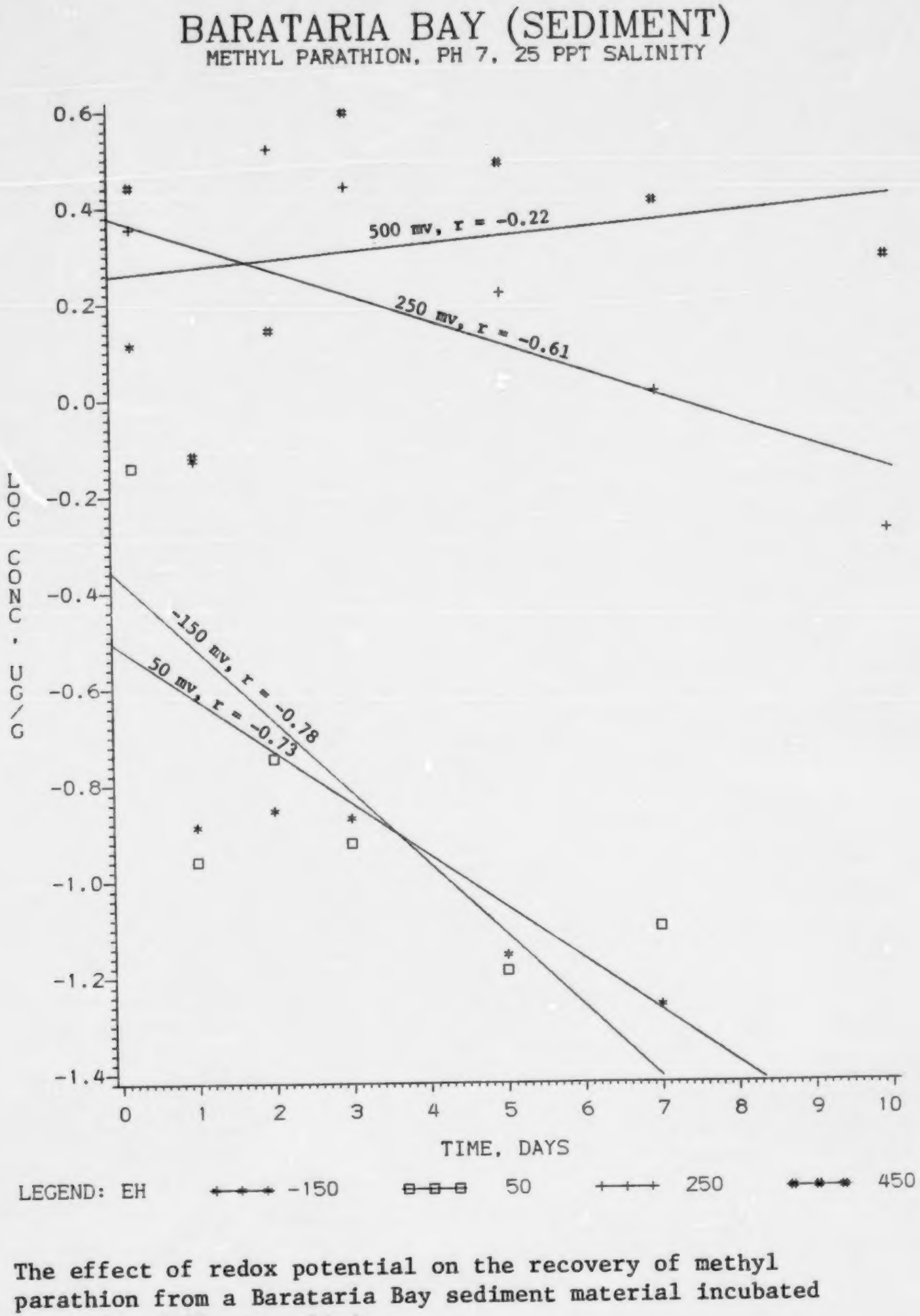

Figure 23. The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 7 and 25 ppt salinity.

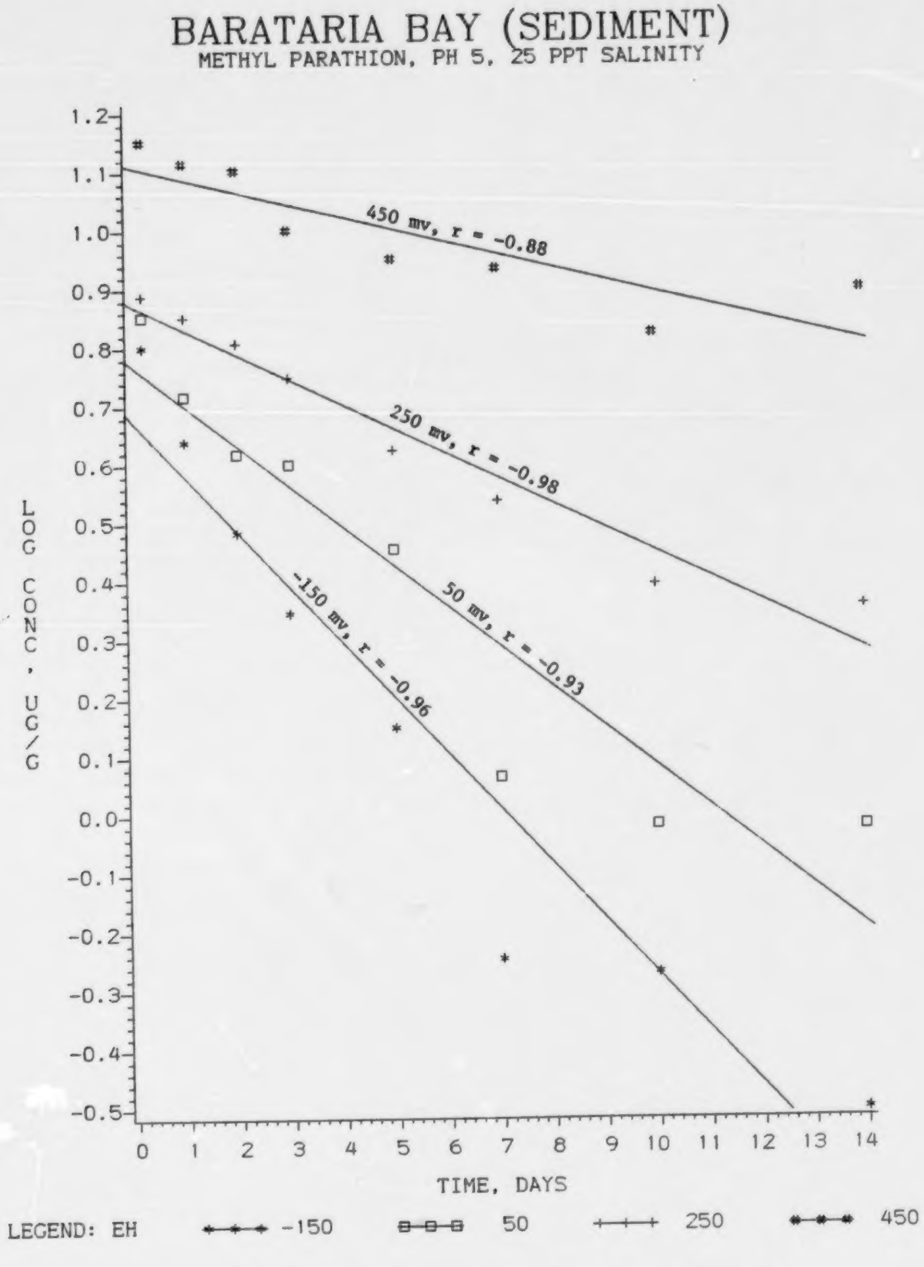

Figure 24. The effect of redox potential on the recovery of methyl parathion from a Barataria Bay sediment material incubated at pH 5 and 25 ppt salinity.

sediment material, and again, redox potential effects are apparent. At pH 5.0, the same response to redox potential is observed, but the compound is considerably more persistent as measurable levels are still present at 14 days under strongly reducing conditions and approximately 50 percent of spiking levels remain under the most oxidizing conditions.

Figures 20 and 21 give the recovery of methyl parathion from the Hartwell Reservoir sediment material incubated at pH 7 and 5 respectively. The same large response to pH and redox potential observed in the previous materials was found with the Hartwell Reservoir sediment material. However, recovery did decrease more rapidly in this material than in the others studied.

Figure 22 shows the recovery of methyl parathion from a Cecil soil incubated at pH 7.0. As observed in the other materials studied, methyl parathion levels decreased most rapidly under strongly reducing conditions. After two weeks, recovery was zero or nearly so at all redox potential levels and this was also generally the case for the pH 7 or 8 treatments in the other soil materials.

Salinity effects on methyl parathion degradation--Figures 23 and 24 show the decrease in recovery of methyl parathion from Barataria Bay sediment suspensions incubated at pH 7 and pH 5, but with a salinity level of 25 ppt instead of 8 ppt as was the case for Figures 18 and 19. At pH 7, the decrease was more rapid initially at the higher salinity level, but the salinity effects were less with time and at 10 to 11 days there was essentially no difference. At pH 5.0, the higher salinity treatment tended to result in a slightly slower reduction in methyl parathion recovery with time, but again, after 10 to 14 days, any differences in levels, if real, were small.

These results indicate that salinity levels may have less effect on the degradation of methyl parathion than pH and redox potential.

The very rapid decrease in recovery of methyl parathion under reduced conditions should be addressed. At -150 mv in the Calcasieu River and Barataria Bay sediments materials, much more than half of the methyl parathion added was not recovered after 0.2 days into the incubation. In the Hartwell Reservoir material, measurable levels were not recovered in sample aliquots taken within minutes after spiking the stirred suspensions. This results in the plots of log concentration vs. time appearing to intercept the Y-axis at significantly different points. However, this was not the case as all suspensions were spiked at the same level. These loss rates seem too fast for microbial degradation. Since the initiation of this project, Whalid et al. (1980) have reported the instantaneous degradation of parathion in anaerobic soils. They reported equilibration of parathion with one prereduced soil resulted in the concentration of the parent molecule decreasing to 44 and 11.6 percent of the original level after 5 second- and 30 minute-equilibrations, respectively. Soil enzymes and/or other heat-labile materials produced under anaerobic, but not aerobic, conditions were implicated. Parathion and methyl parathion are similar enough such that this process reported for parathion may be a contributing factor in the very rapid disappearance of methyl parathion in the anaerobic soil and sediment materials in this study.

If the data points of log concentration vs. time are linear, first order degradation kinetics are suggested. In a few cases, the correlation coefficients are low indicating poor linearity (in particular, the Barataria Bay experiment at pH 7, 25 ppt salinity). Many of the remaining correlation coefficients were high suggesting a reasonably good fit to a straight line (21 out of the remaining 29 regression lines had an r value of -.88 or better). However, most of the methyl parathion plots curved upward toward the end of the incubations indicating processes are involved giving some deviation from simple first order kinetics. With the exception of the incubation represented by Figure 23 in which there appeared to be excessive experimental variability, the lowest measurable concentration value was consistently above the regression line (24 of 27 regression lines consisting of 3 or more points). The reasons for this deviation from linearity and first order degradation kinetics were not pursued further at this time.

2,4-D--Figure 25 shows the recovery of 2,4-D from a Cecil A horizon (topsoil) material incubated at pH 7 and four redox potential levels. As observed for methyl parathion, redox potential affects the loss of 2,4-D. However, unlike methyl parathion, this compound is removed more rapidly from oxidized soil materials than reduced soil. From an initial spiking level of 12 to 15 ppm, 0.3 to 0 ppm were recovered after two weeks at the two highest oxidation levels, but about half of the material (greater than 6 ppm) remained in the soil at the two most reducing redox potential levels.

This agrees with the work of Liu et al. (1981) who, working with laboratory cyclone fermentors, reported the half-life of 2,4-D was near 40 times greater under anaerobic as compared to aerobic conditions.

A plot of log concentration vs. time was near linear for the two most oxidizing treatments (r = -0.88 and -0.96 for 500 and 250 mv respectively), while the remaining two redox potential treatments gave low correlation coefficients, apparently due to experimental variability.

Aroclor 1254--Aroclor 1254, one PCB formulation, was incubated with Hartwell Reservoir sediment material at 2 pH levels (Figures 26 and 27). These incubations were carried out for just over six weeks. The levels of amended Aroclor 1254 generally decreased to just under half of the spiking levels after six weeks. There appeared to be no strong pH or redox potential effects on the recovery of this PCB formulation.

At pH 6, and for three of the four treatments plotted at pH 7, the slopes of the regression lines were very similar. Only the 250 mv regression line may have had a significantly different slope, and this was mostly due to apparent experimental variability in one or two data points. All but the pH 7, 250 mv treatment gave a good fit to a straight line as indicated by regression coefficients of -0.96 or better.

CO_2 Evolution as an Indication of Microbial Respiration--

Microbial degradation is believed to be the primary process by which many synthetic organics are broken down and removed from the

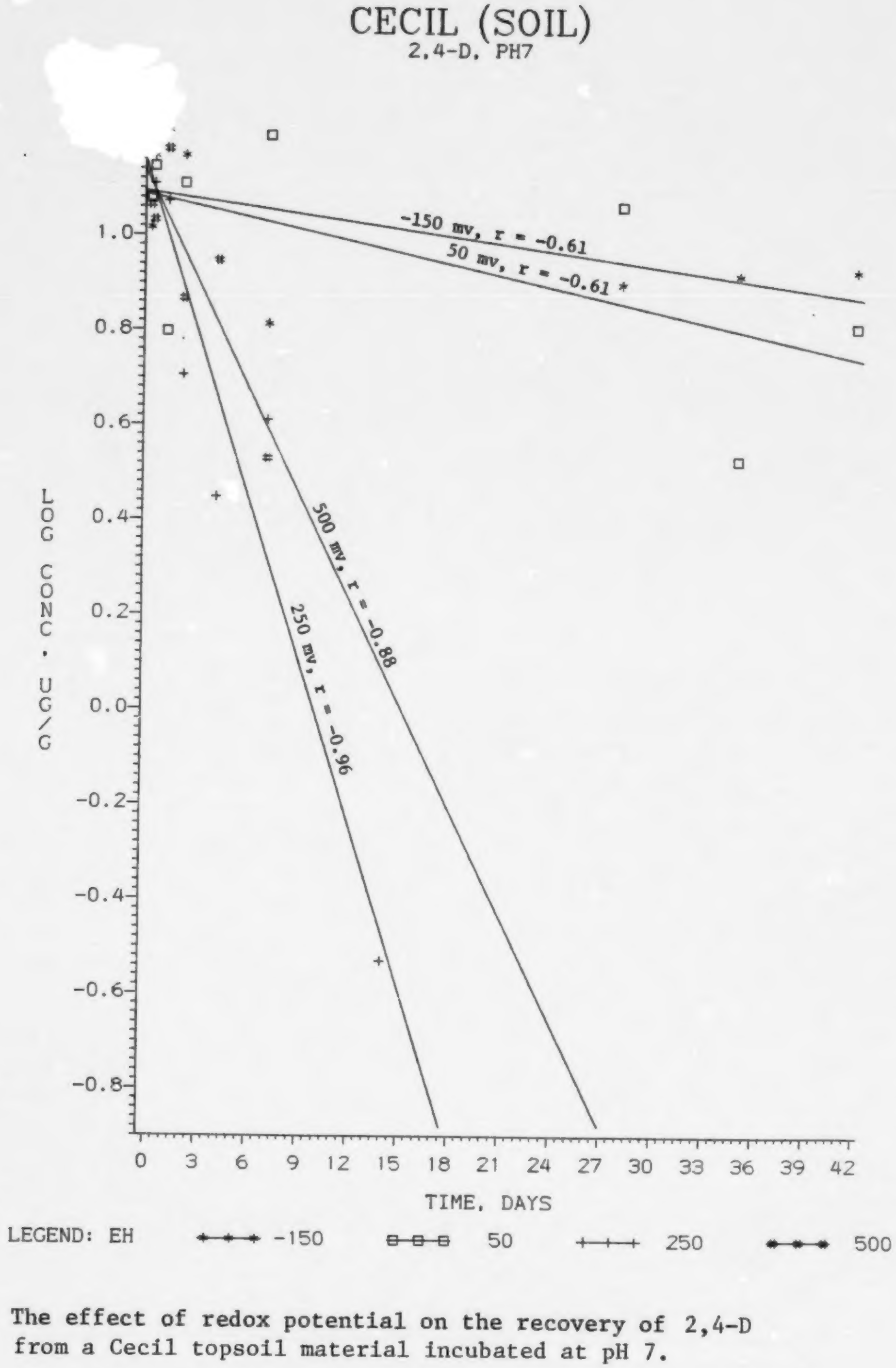

Figure 25. The effect of redox potential on the recovery of 2,4-D from a Cecil topsoil material incubated at pH 7.

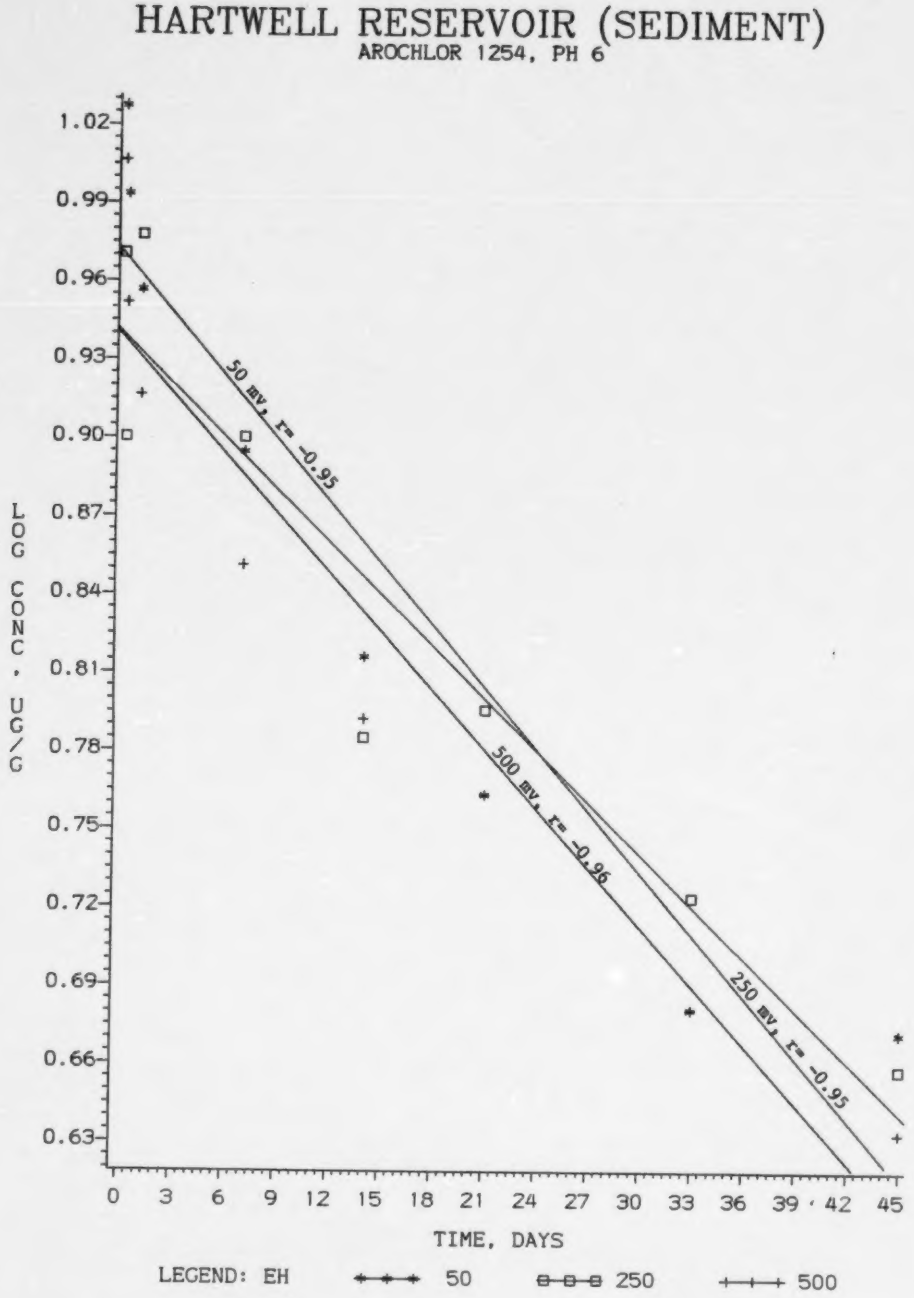

Figure 26. The effect of redox potential on the recovery of Aroclor 1254 from a Hartwell Reservoir sediment material incubated at pH 6.

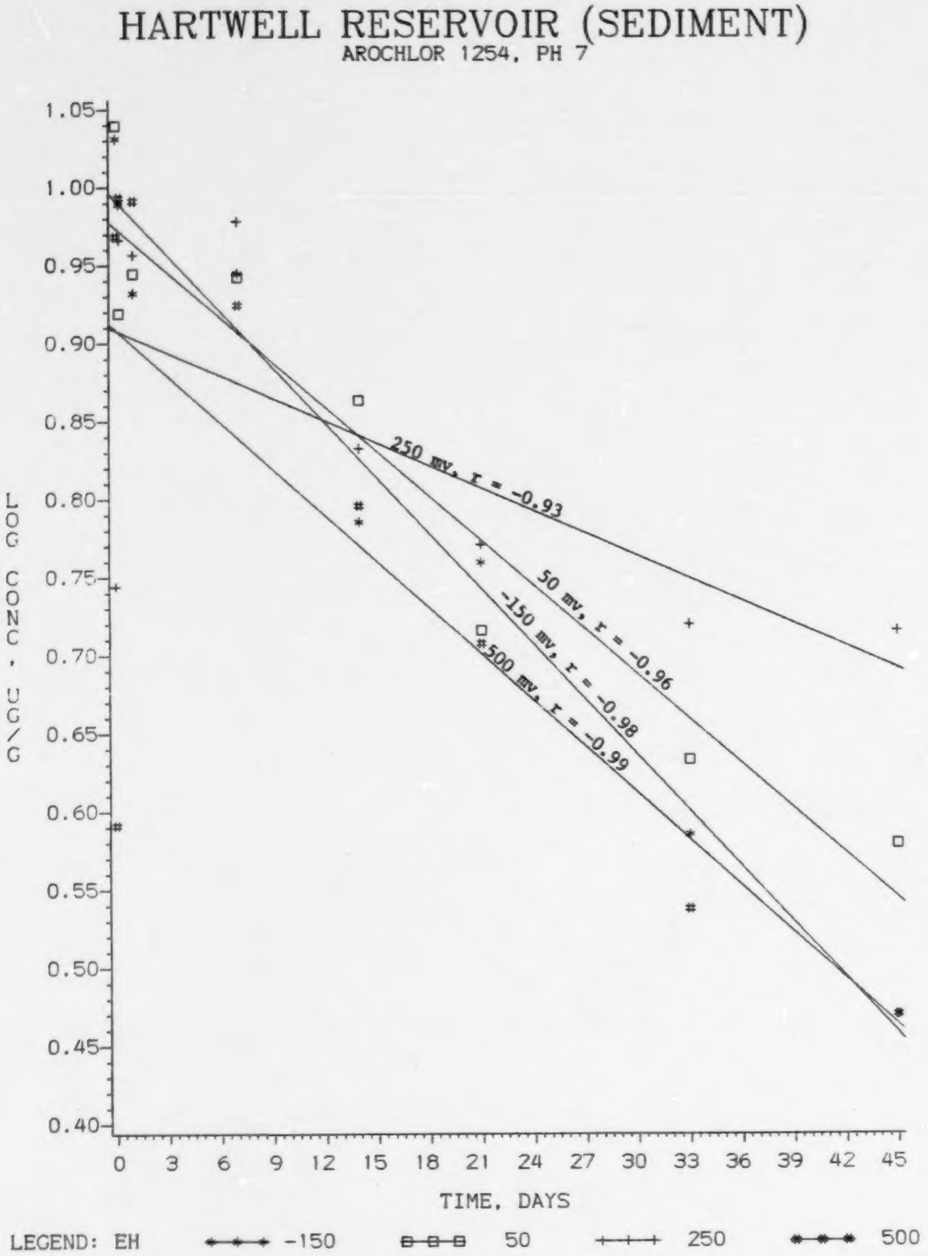

Figure 27. The effect of redox potential on the recovery of Aroclor 1254 from a Hartwell Reservoir sediment material incubated at pH 8.

environment. This project and similar work has demonstrated that oxidation-reduction conditions do affect the degradation rate of many synthetic organics. Oxidation-reduction conditions also affect the types of microorganisms that will be active and certain metabolic processes such as what oxidants are used for terminal electron acceptors in the case of facultative anaerobic organisms. Thus it would be of interest to know the relative microbial respiration rates in the laboratory microcosms used to study degradation of synthetic organics under controlled pH and redox potential conditions. This was accomplished by scrubbing CO_2 from inlet streams of the nitrogen purge gas and the air additions used to control oxidation levels in selected experiments, then measuring the total carbon dioxide evolved. The primary source of this carbon dioxide would be soil or sediment humic material being mineralized by microbial respiration. In some cases, microcosms for all redox potential levels were amended with ground rice straw in attempts to achieve the low end of the desired redox potential range. At certain of the sampling intervals, there were some problems with leaks, apparent carbonate precipitation, or other unexplained anomalies. Nevertheless, the data generally indicate greater microbial activity with increasing redox potential. The results are given in Figures 28 through 31. A few problems were encountered in attempting to continuously collect all of the CO_2 produced by each flask over extended periods of time. Table 6 gives some information on the problems encountered and some additional notes on this study. Though some problems were evident, it is apparent from examining Figures 28 through 31 that microbial activity as measured by CO_2 production was greatest under well oxidized conditions. The total CO_2 evolved at -150 and 50 mv ranged from 11 to 30 percent of that evolved at 500 mv in the four experiments. This is in close agreement with the results of DeLaune et al. (1981) who measured pH and redox potential effects on $^{14}CO_2$ produced in soil suspensions amended with ^{14}C-labeled plant material. Considering these results and the redox effects on degradation rates, it is clear that one cannot make the blanket statement total microbial respiration accounts for the redox potential effects on the degradation of synthetic organics in general and methyl parathion in particular in this study. While this could be true for a few specific organics, this research shows the degradation of two of the three compounds studied to behave independently of total microbial respiration. The most rapid loss in recovery of methyl parathion occurred where the respiration rate is lowest (reducing conditions) and the degradation of Aroclor 1254 was not appreciably affected by either redox potential or respiration rates. The degradation rate of 2,4-D corresponded in a general way with increasing respiration rate and redox potential, but it is not possible from these data to say definitely what the influence of respiration rate was on 2,4-D degradation, or even to state that there is a cause and effect relationship between respiration and degradation rate.

Biometer Flasks Using Mineralization Rate of ^{14}C-Labeled Compounds for Analysis

The primary advantages of the biometer flask approach for degradation studies are their simplicity and low cost. Compared to the controlled pH-redox potential microcosms, the biometer flasks, using collection of $^{14}CO_2$ as an indication of degradation, permit the study of a larger

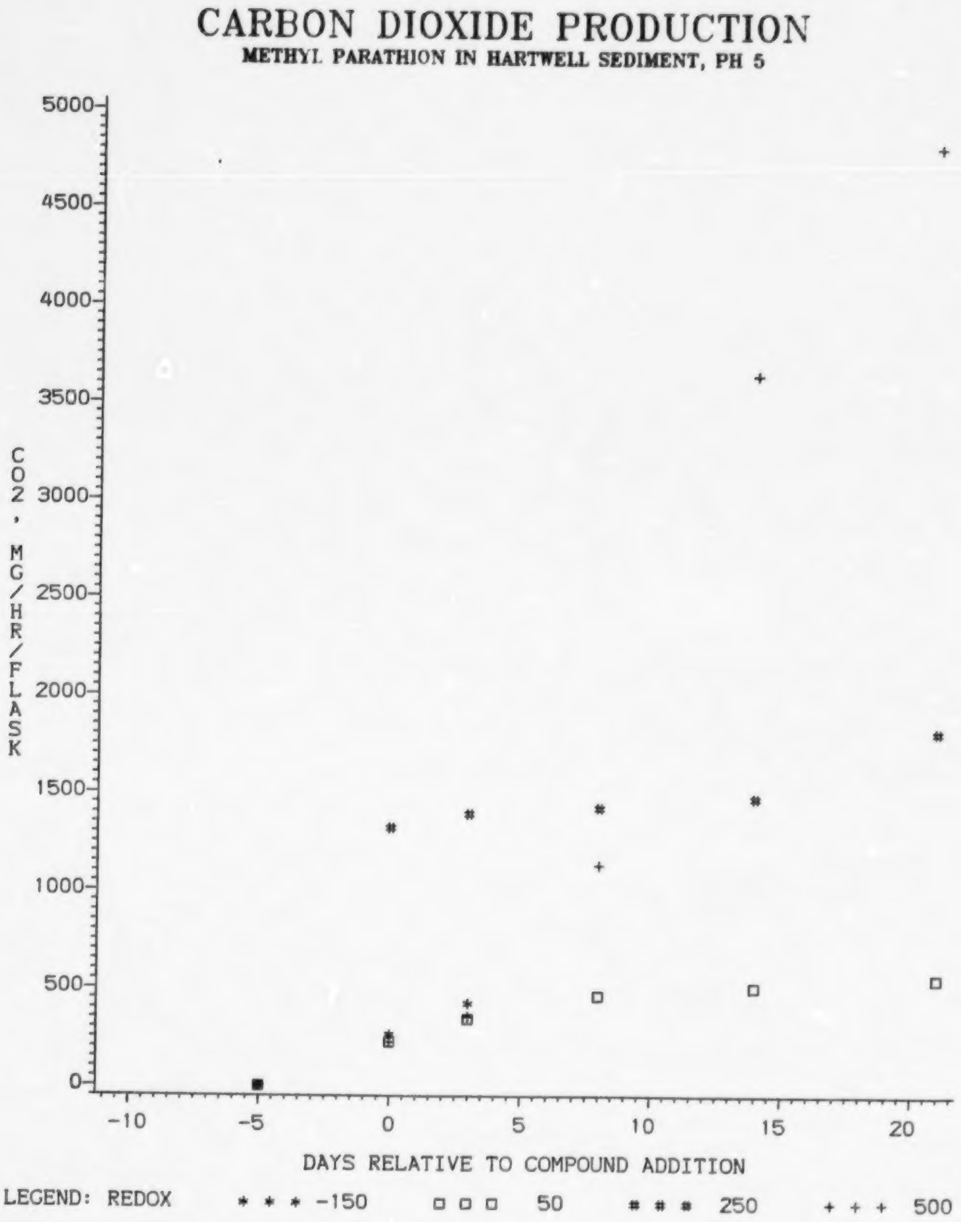

Figure 28. Carbon dioxide production as an indication of relative microbial activity in a methyl parathion-amended Hartwell Reservoir sediment material incubated at four redox potential levels at pH 5.0.

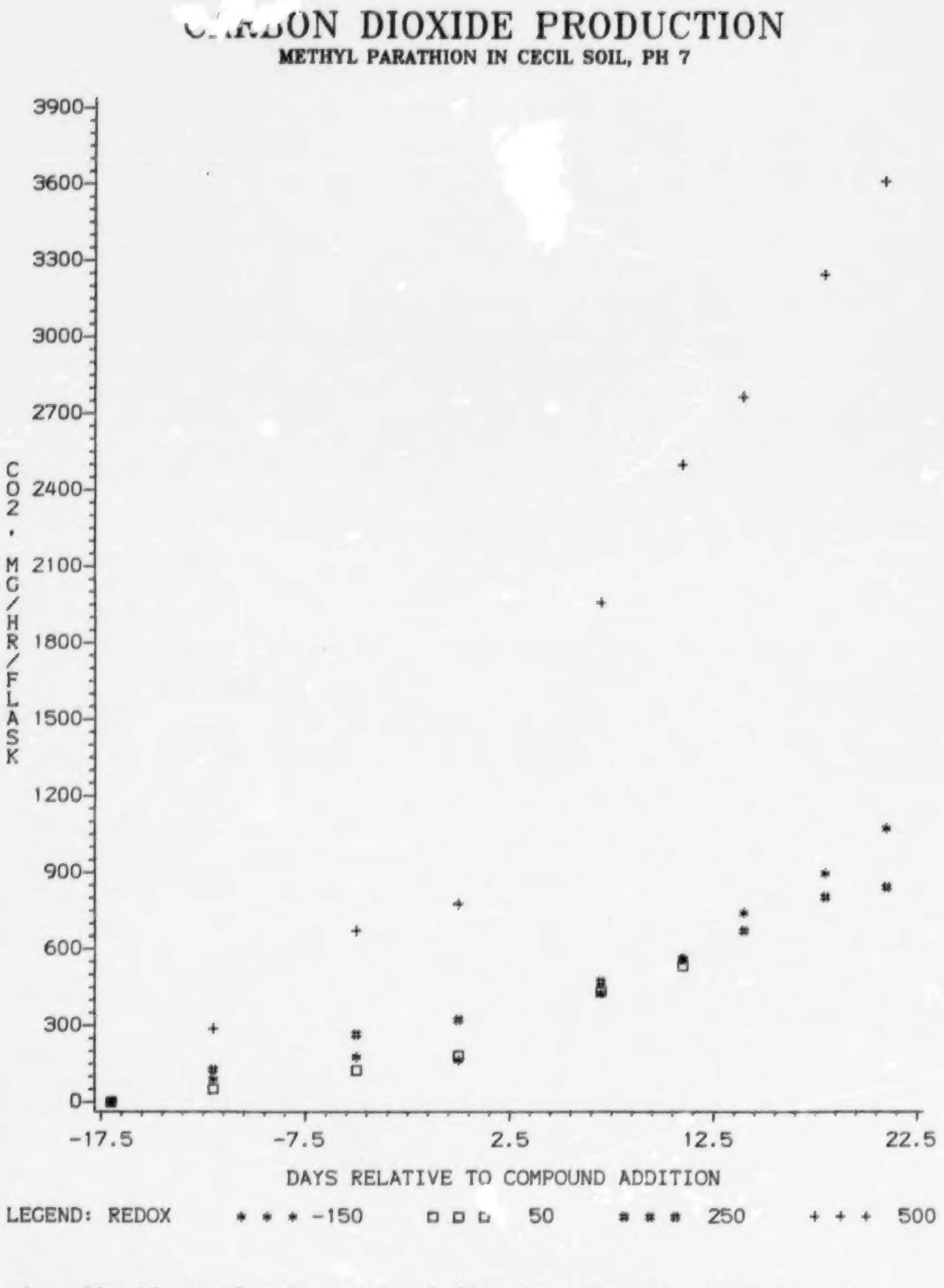

Figure 29. Carbon dioxide production as an indication of relative microbial activity in a methyl parathion-amended Cecil topsoil material incubated at four redox potential levels at pH 7.0.

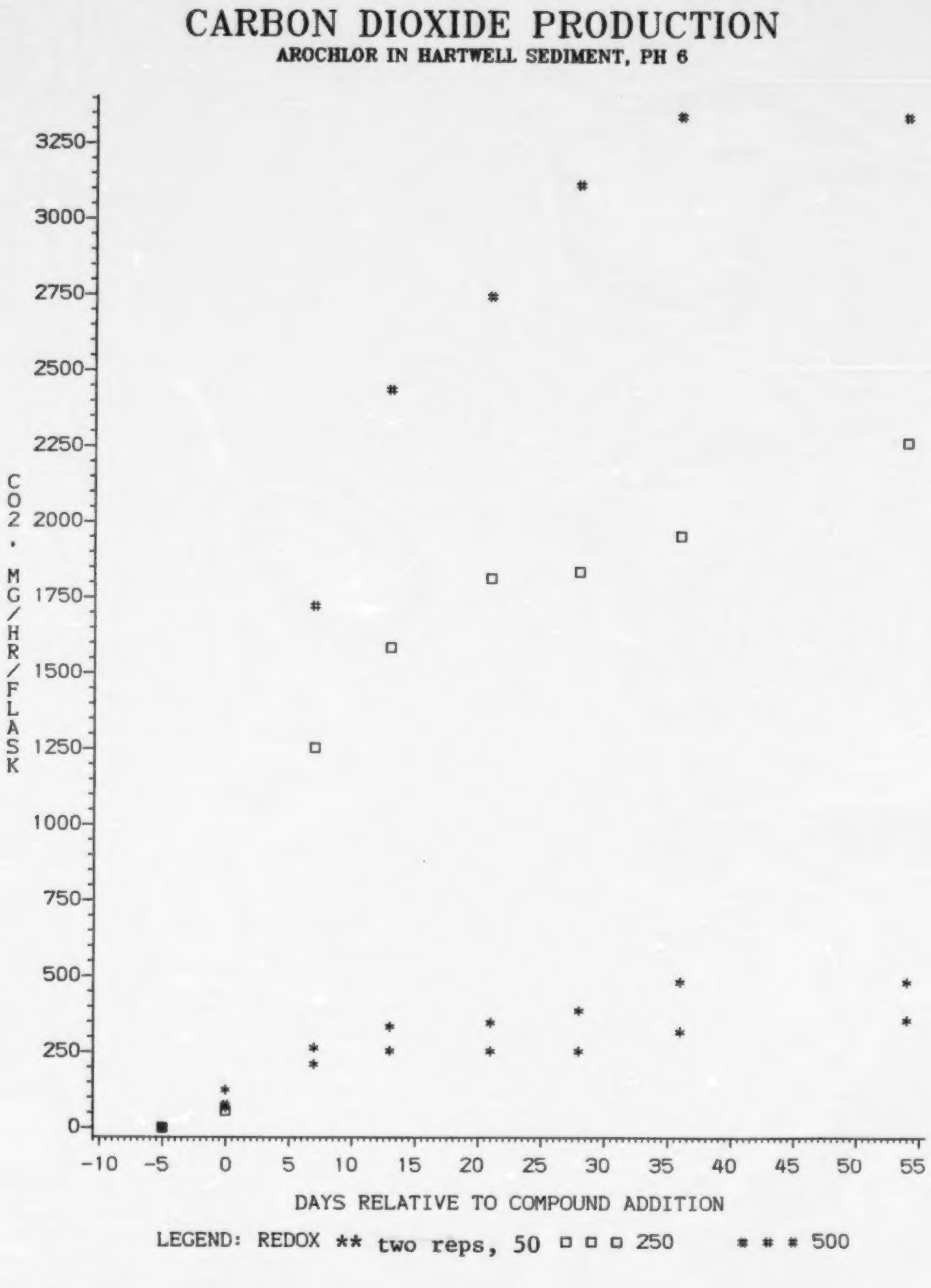

Figure 30. Carbon dioxide production as an indication of relative microbial activity in an Aroclor 1254-amended sediment material incubated at pH 6 and four redox potential levels.

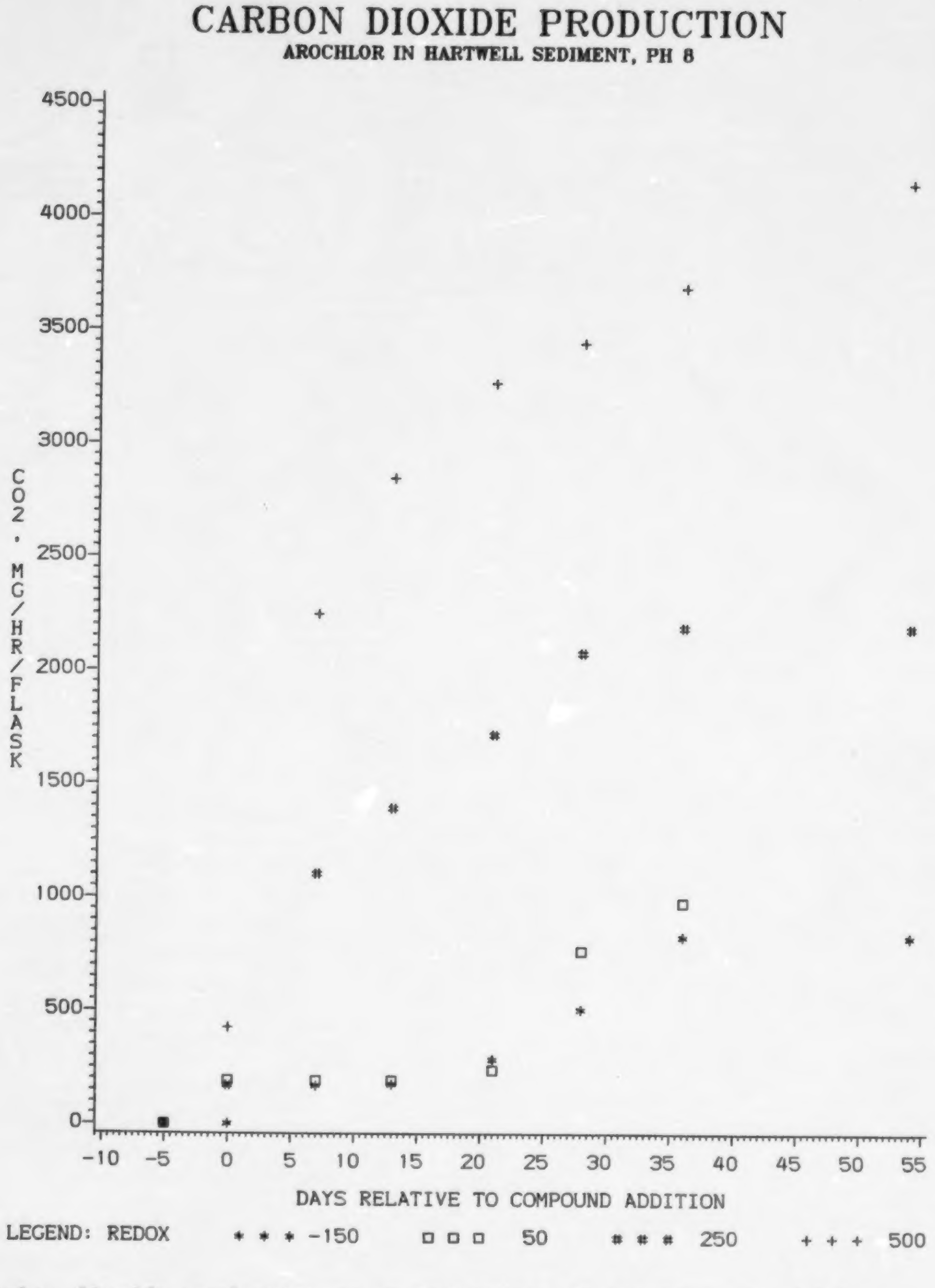

Figure 31. Carbon dioxide production as an indication of relative microbial activity in an Aroclor 1254-amended sediment material incubated at pH 8 and four redox potential levels.

TABLE 6. NOTES ON CARBON DIOXIDE COLLECTION STUDIES TO INDICATE RELATIVE MICROBIAL RESPIRATION

Corresponding Figure	Interval, days[1]	Redox potential, mv			
		-150[2]	50	250	500
28(Hartwell, pH 5 methyl parathion)	-5 to 0			← precipitate formed in trap	
	0 to 3				
	3 to 8	← leaks developed ↓			
"	8 to 14				← traps were saturated
"	14 to 21				
29(Cecil, pH 7 methyl parathion)	-17 to -12	<—— 2 grams ground rice straw added ——>			
	-12 to -5				
	-5 to 0	<—— changed from 0.1 to 0.2N NaOH in traps ——>			
"	0 to 7	<—— 2 grams ground rice straw added ——>			
"	7 to 11				
"	11 to 14		← leak developed ↓		
"	14 to 18				
"	18 to 21				
30(Hartwell, pH 6, Aroclor 1254)	-5 to 0				
	0 to 7				
	7 to 13				
	13 to 21	← precipitate formed in trap			
	21 to 28				
	28 to 36				
	36 to 54				
31(Hartwell, pH 8, Aroclor 1254)	-5 to 0				
	0 to 7				
	7 to 13				
	13 to 21				
	21 to 28				
	28 to 36				
	36 to 54		← leaks developed		

---

[1] Relative to time samples were amended with a synthetic organic.

[2] Redox potential was 50 mv for Figure 30 (Hartwell, pH 6.0, Aroclor 1254).

number of experimental parameters with adequate replication. Since a primary objective of this research was to examine redox potential effects on degradation of synthetic organics in several soil and sediment materials, we made extensive use of this experimental approach. It should be noted, however, that this experimental method measures mineralization of the labeled portion of the molecule rather than simple modification of the parent compound. This difference will be discussed more thoroughly elsewhere in this report.

Methyl Parathion--

Figures 32 through 37 indicate the recovery of ^{14}C-labeled carbon dioxide from the degradation of methyl parathion in six soil and sediment materials. There was a very large and statistically significant oxidation treatment effect in all six materials. In every case after the two to three month incubations, 10 to 20 times or more of the labeled carbon was evolved as labeled CO_2 under oxidized conditions compared to reducing conditions. Also, soil properties greatly affected recovery of methyl parathion as collected labeled carbon ranged from about 0.7 to 3.2 and 13 to 87 percent of that added for the reduced and oxidized treatments respectively. In the oxidized materials, there appears to be some association between mineralization of the methyl parathion and pH. In all but the Hartwell Reservoir material, the evolution of labeled carbon dioxide had leveled off or decreased to a slow rate at the end of the incubation compared to earlier in the incubation.

Although much smaller accumulations of labeled CO_2 were observed from the reduced treatment when the studies were terminated, all but the Lake Providence material was still producing labeled carbon dioxide at the highest rate observed when the experiments were terminated (a leveling off of labeled carbon dioxide production had not occurred in the reduced treatments).

Upon examination and comparison of the controlled pH-redox potential microcosm results and the biometer flask results, two major differences are readily apparent: (1) the apparent degradation rate of methyl parathion is much slower in the unstirred soil suspensions, and (2) the redox potential treatment effects are opposite using the two techniques. These observations must be addressed.

Regarding the rate of degradation, the biometer flasks were maintained at about 23°C whereas the stirred suspensions were kept at about 28°C. This temperature difference would be expected to contribute to some increase in degradation rate in the stirred suspensions. Also, Parr and Smith (1974) noted a similar stirring effect in laboratory studies of toxaphene degradation under both aerobic and anaerobic conditions. It was suggested that stirring some soils provides additional available carbon to microorganisms to sustain rapid degradation of toxaphene. Measurements of total carbon dioxide evolution showed there was a higher level of respiratory activity in a stirred anaerobic suspension compared to a moist, unstirred, anaerobic suspension.

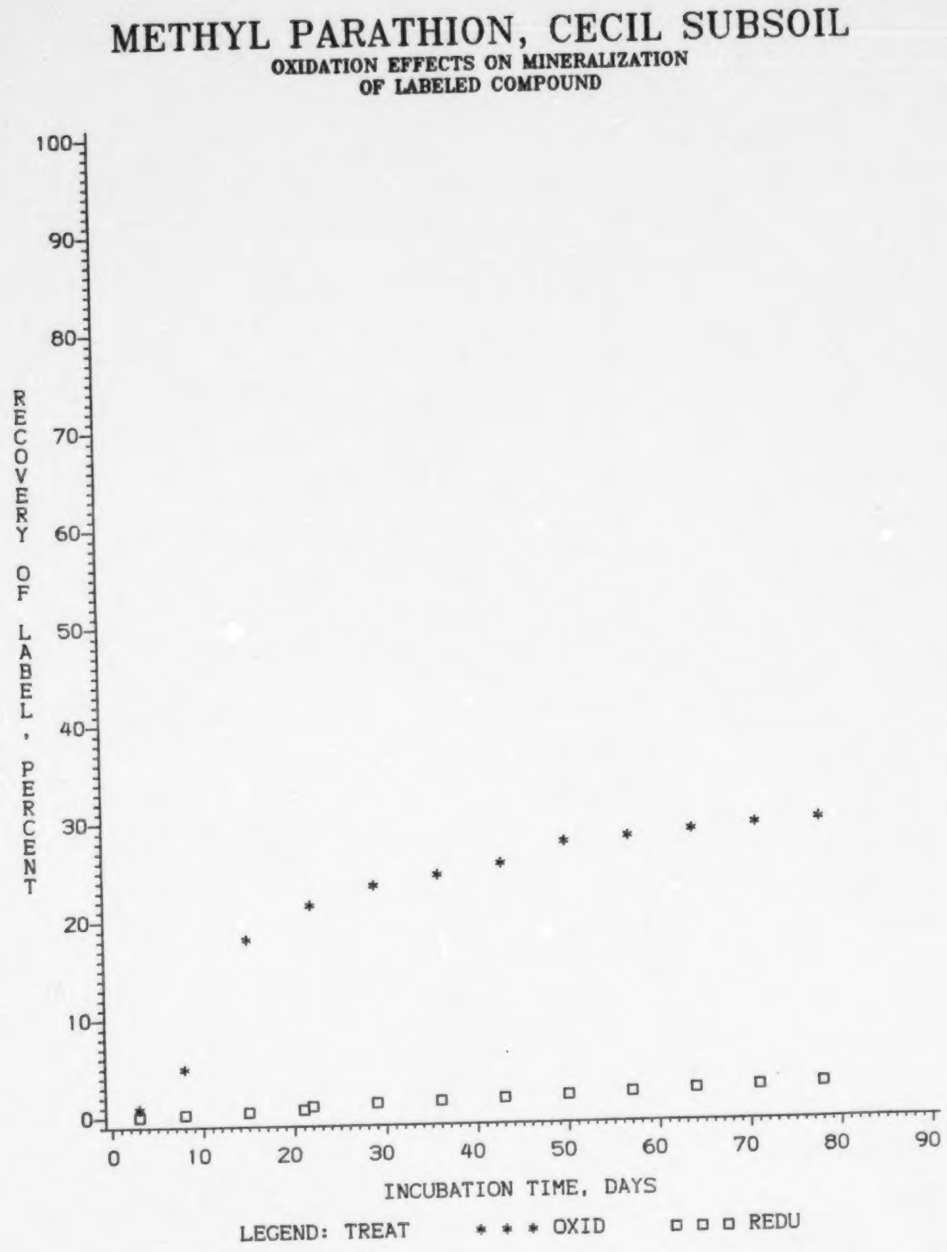

Figure 32. Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil subsoil material.

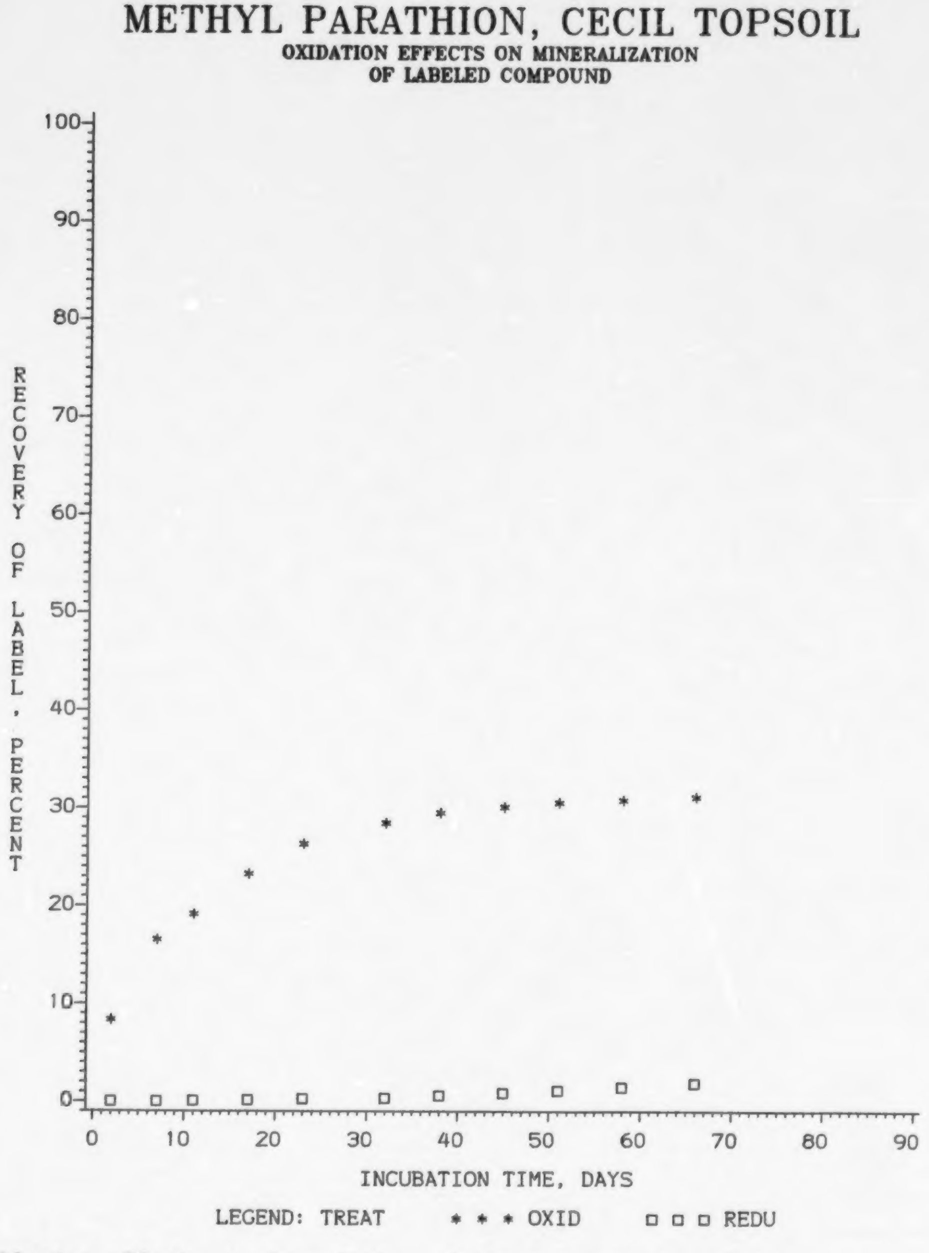

Figure 33. Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil topsoil material.

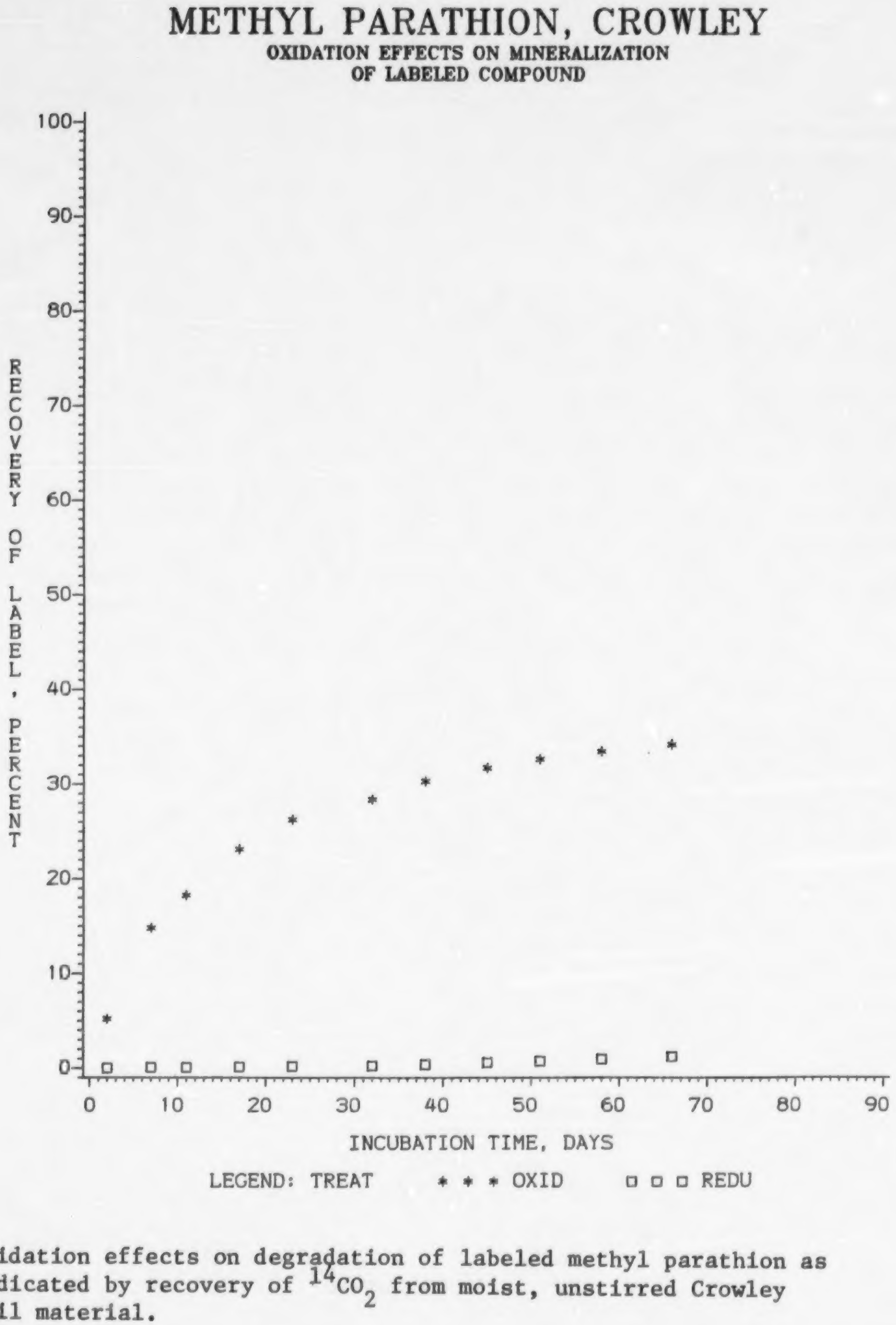

Figure 34. Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Crowley soil material.

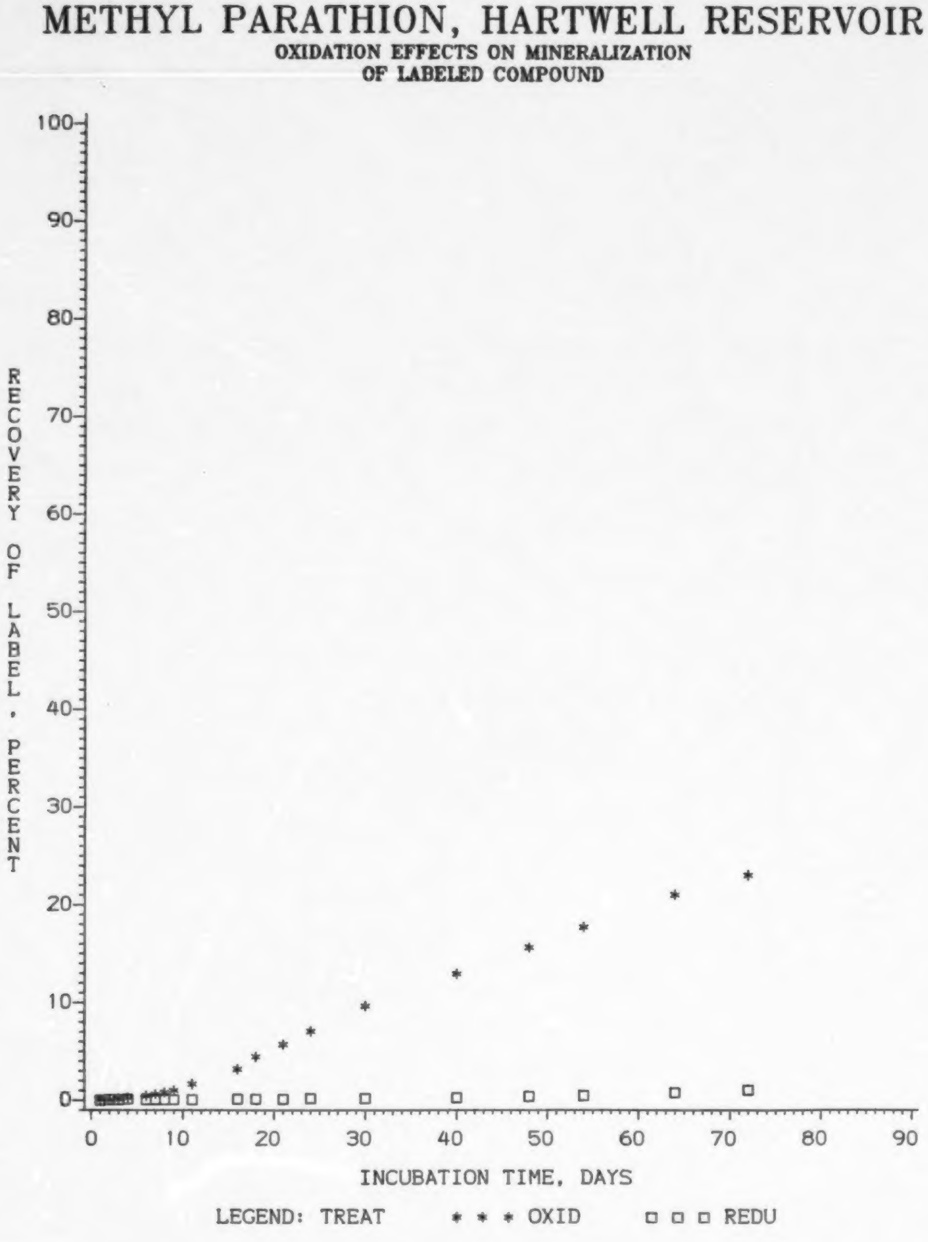

Figure 35. Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Hartwell Reservoir sediment material.

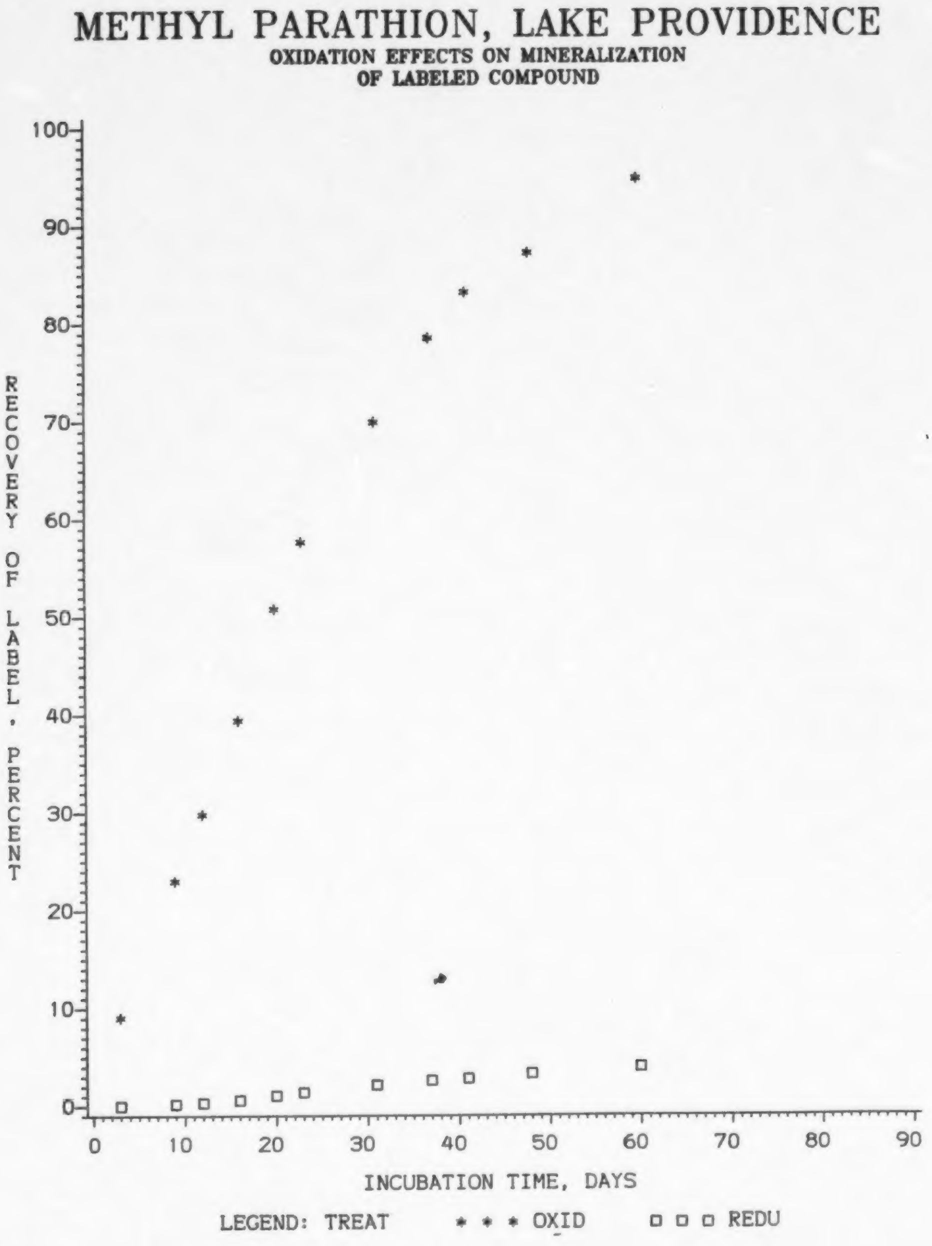

Figure 36. Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Lake Providence material.

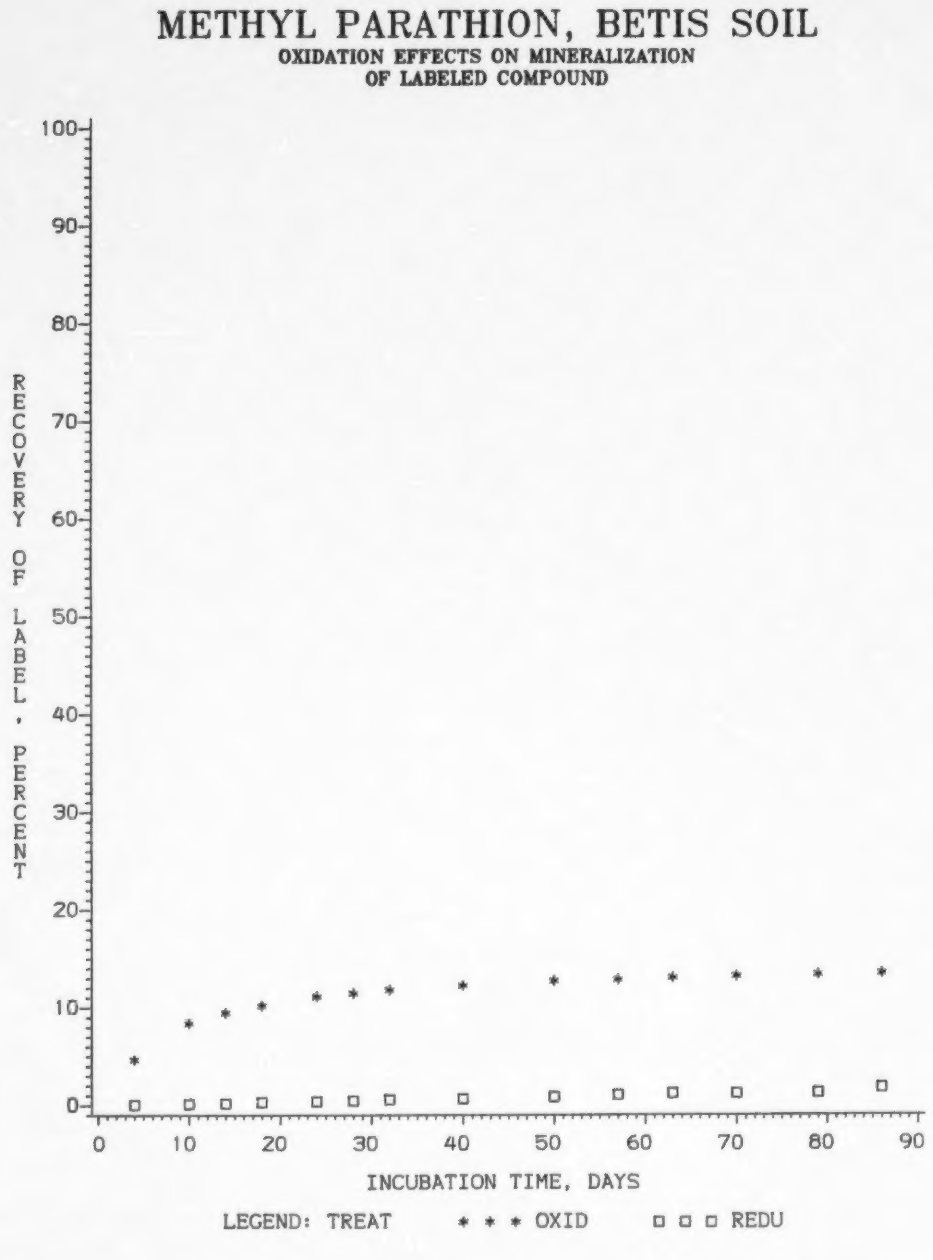

Figure 37. Oxidation effects on degradation of labeled methyl parathion as indicated by recovery of $^{14}CO_2$ from moist, unstirred Betis topsoil material.

In the biometer flask degradation studies, the labeled carbon was located in the aromatic ring of the methyl parathion molecule. Literature discussed elsewhere in this report suggest that several other modifications to the molecule will occur before degradation of the aromatic ring (i.e., hydrolysis of the ester group and reduction of the nitro group on the benzene ring). This recovery of the label as carbon dioxide represents very substantial modification (degradation) of the parent compound. The rate of recovery of the label as CO_2 does not say anything about the rate of initial or partial degradation of the parent compound as several intermediate degradation products are probably involved before mineralization of the aromatic ring to carbon dioxide occurs. Thus it is highly probable that modification of the parent molecule occurred at a greater rate than indicated by the rate of recovery of the label. Extraction of the soil or sediment material and analysis by gas chromatography more accurately indicates the rate of loss of the parent compound, but, unless intermediate degradation products are identified and quantified, does not reveal much about the rate of total mineralization of the parent molecule. Both ^{14}C labeled and extraction/specific compound quantification methods are used extensively in degradation studies of synthetic organics. The comparison of results by the two methods in this study clearly indicate a researcher should carefully consider the compatibility of a particular experimental approach with the research objectives.

2,4-D--

Figures 38 through 44 indicate the recovery of labeled carbon as CO_2 from the same six soil materials used for the biometer flask studies of methyl parathion. As for methyl parathion, it is clearly apparent that both oxidation-reduction conditions and soil/sediment properties affect the mineralization rate of ring-labeled 2,4-D. Recovery of the labeled material as CO_2 ranged from about 0.5 to 35 percent and 10 to 85 percent for the reduced and oxidized treatments, respectively. Surprisingly, the results from the reservoir and lake sediments were essentially on opposite ends of the recoveries obtained for the six soil and sediment materials. Both are fine textured sediments with moderate amounts of organic matter. No simple relationship is apparent between the percentage recovery of the label and soil properties measured. There is likely a complex interaction between soil properties contributing to the observed rates of mineralization that might require a larger number of soil and sediment materials to identify.

The controlled pH-redox potential microcosm studies also indicated the parent compound was degraded more quickly under oxidizing conditions. As expected, the initial modification of the parent material occurred more quickly than mineralization of the aromatic ring. For example, in the two oxidized treatments of the Cecil topsoil extracted and analyzed by gas chromatography, none of the parent molecule was recovered after four weeks while 90 percent of the label had not been recovered from the oxidized biometer flask after about 11 weeks. Again, at least two processes are probably involved with these differences: 1) initial and subsequent molecular modifications through intermediates may be faster under stirred rather than unstirred conditions, and, 2) recovery of

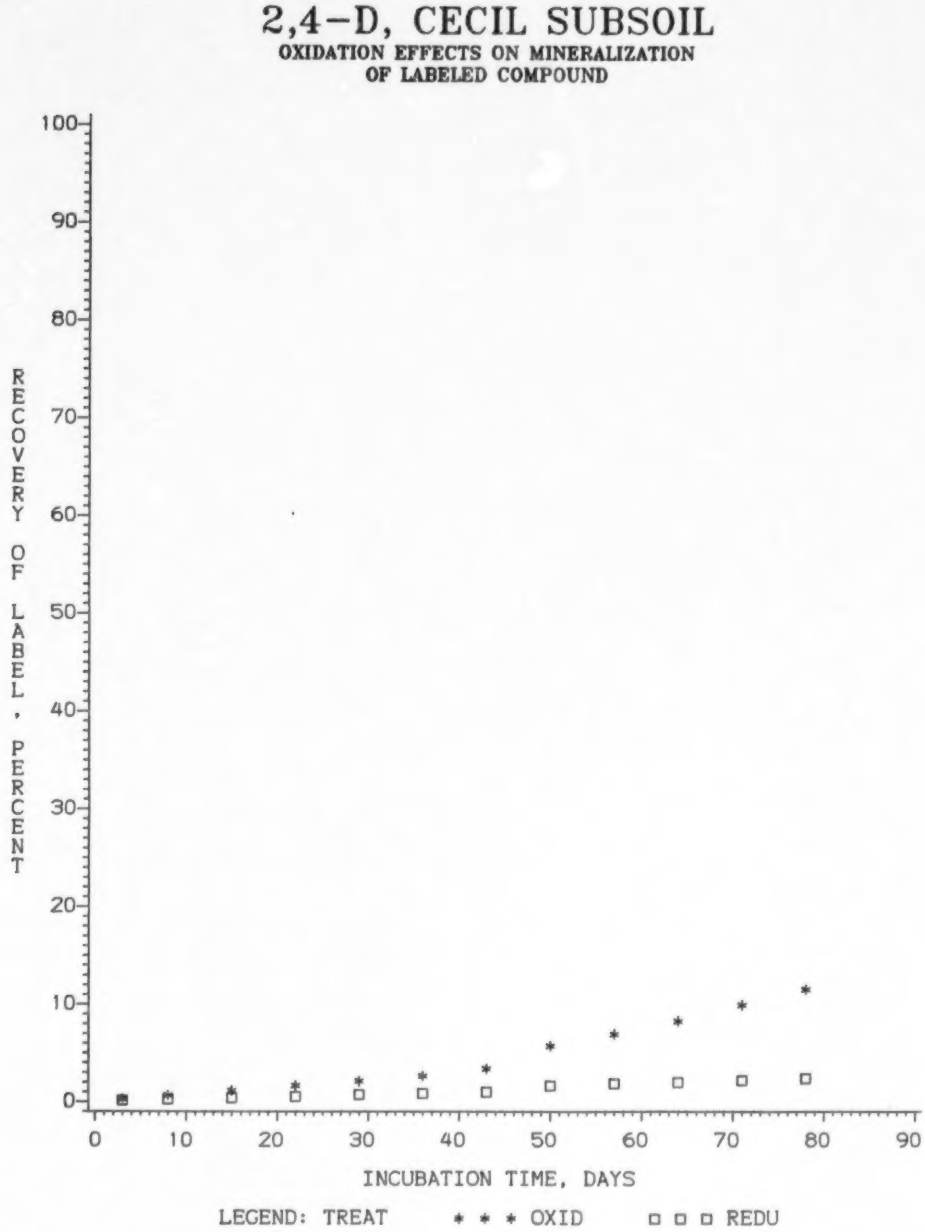

Figure 38. Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil subsoil material.

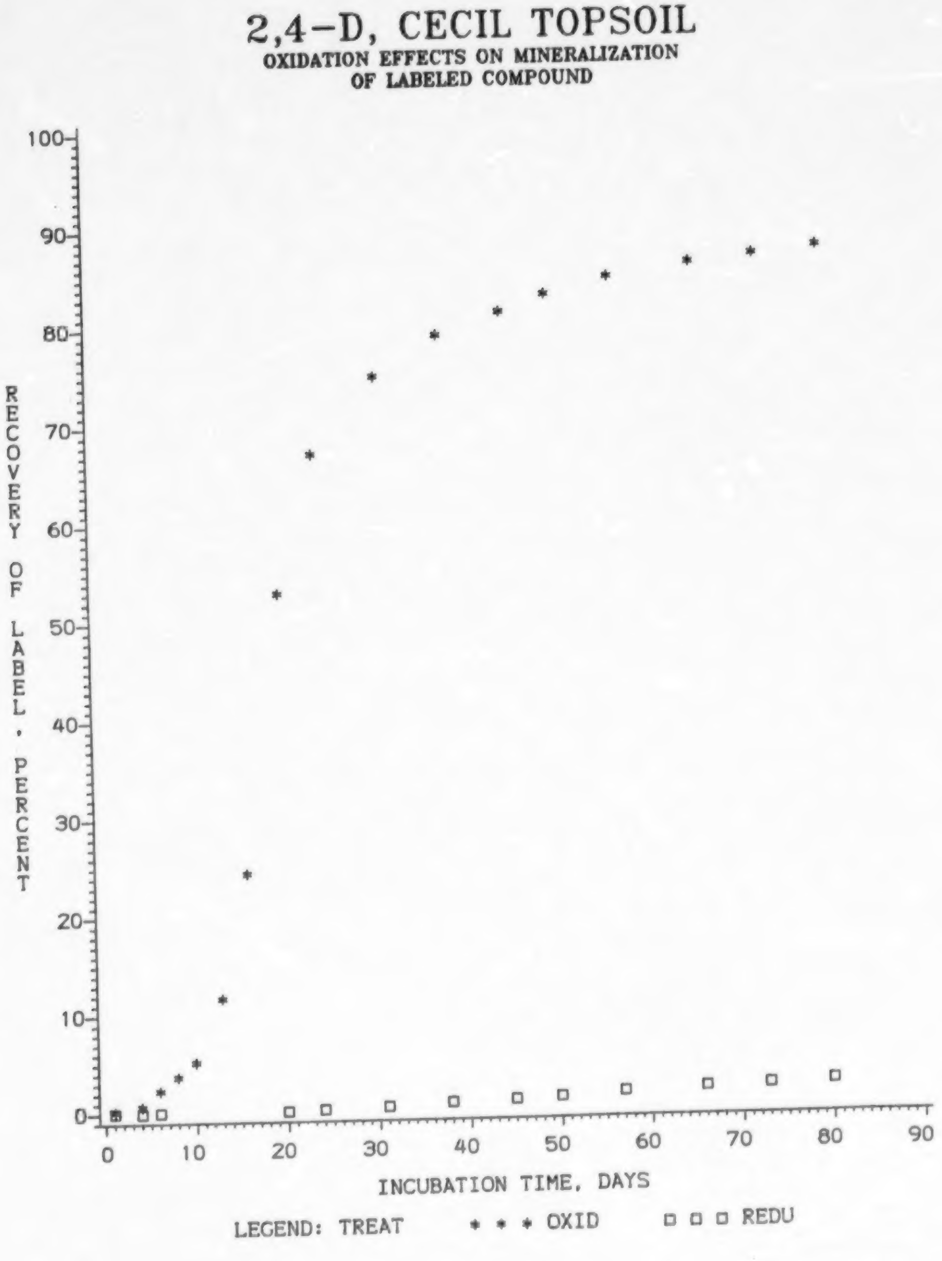

Figure 39. Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil topsoil material.

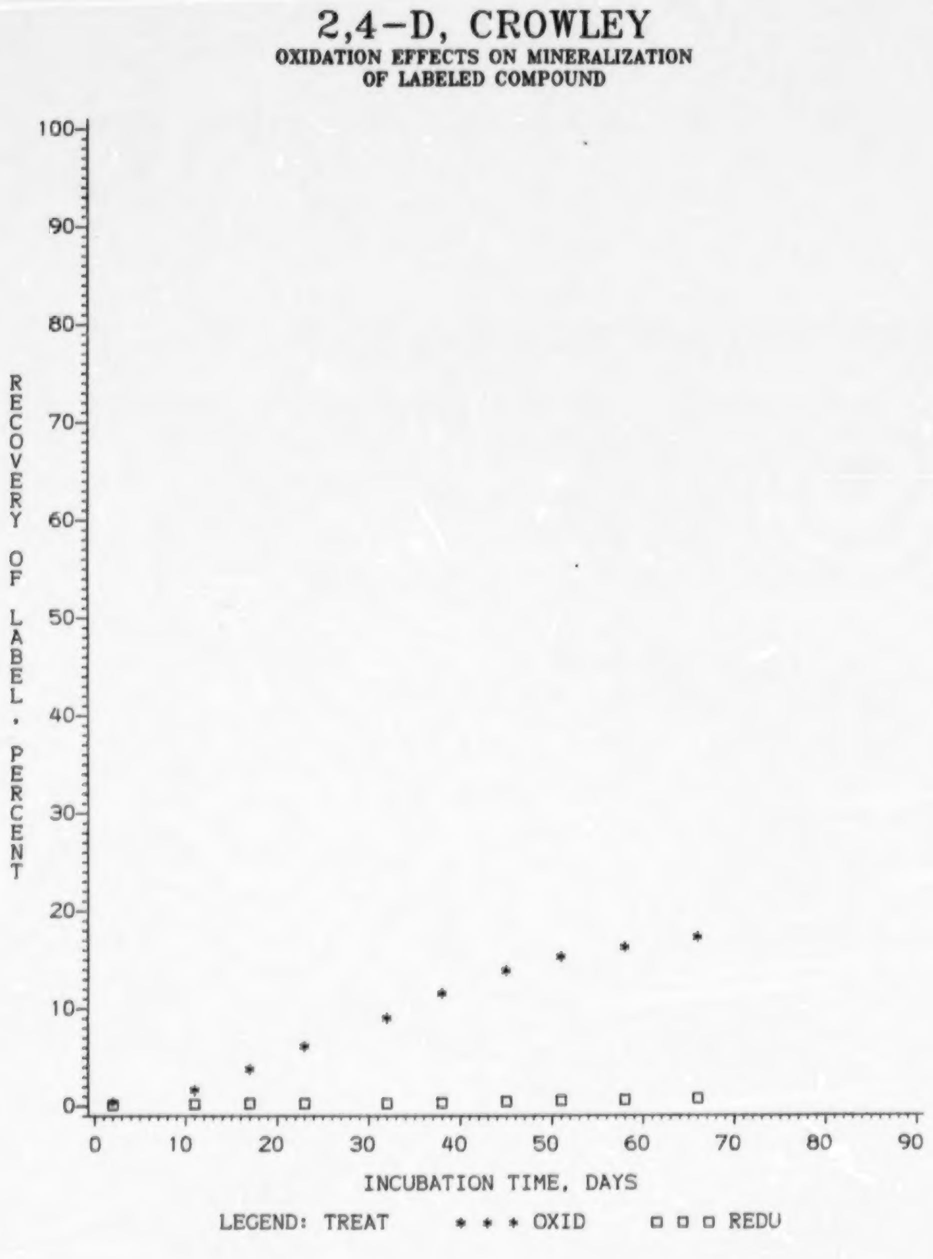

Figure 40. Oxidation effects on degradation of labeled 2,4-D as indicated as indicated by recovery of $^{14}CO_2$ from moist, unstirred Crowley topsoil material.

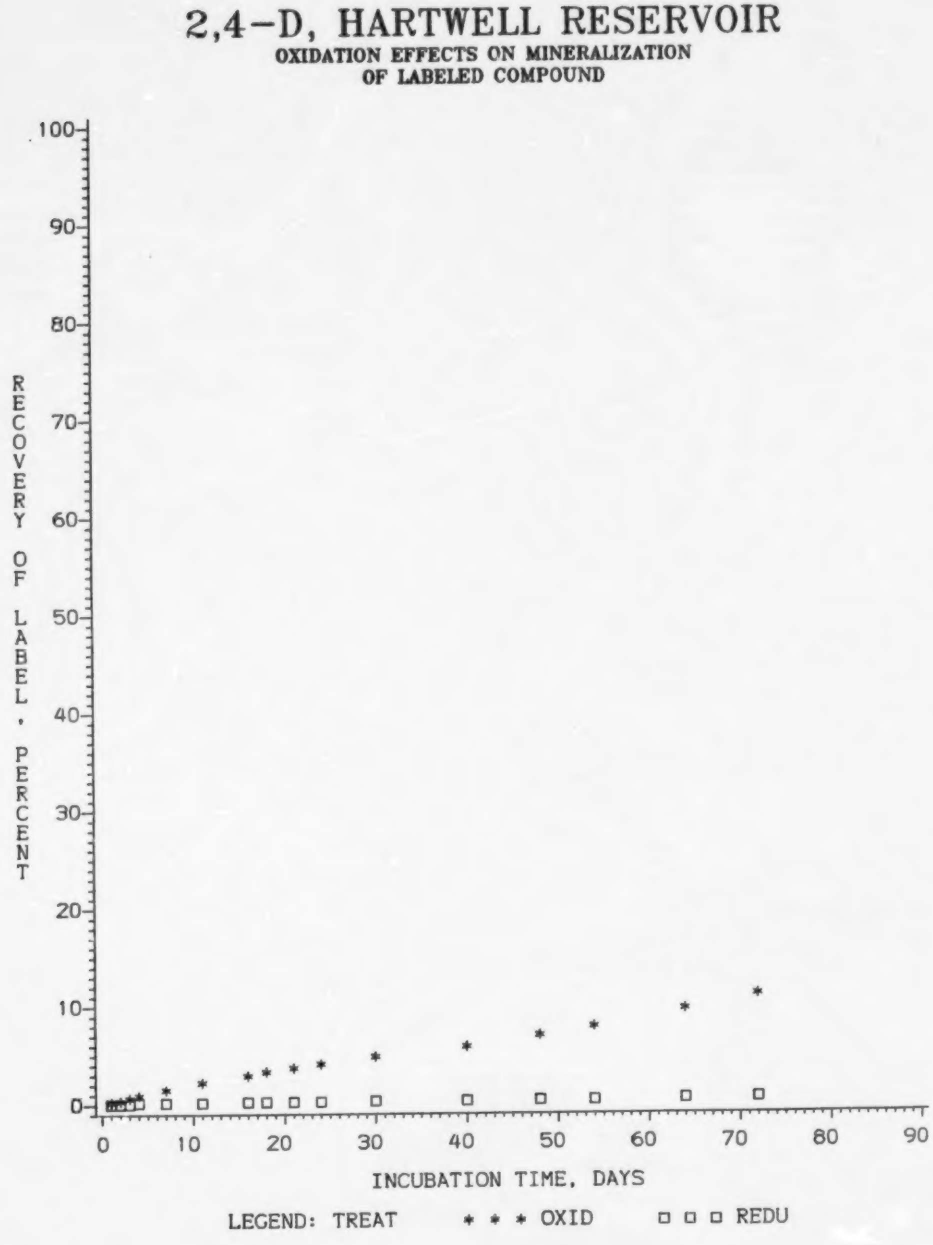

Figure 41. Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Hartwell Reservoir sediment material.

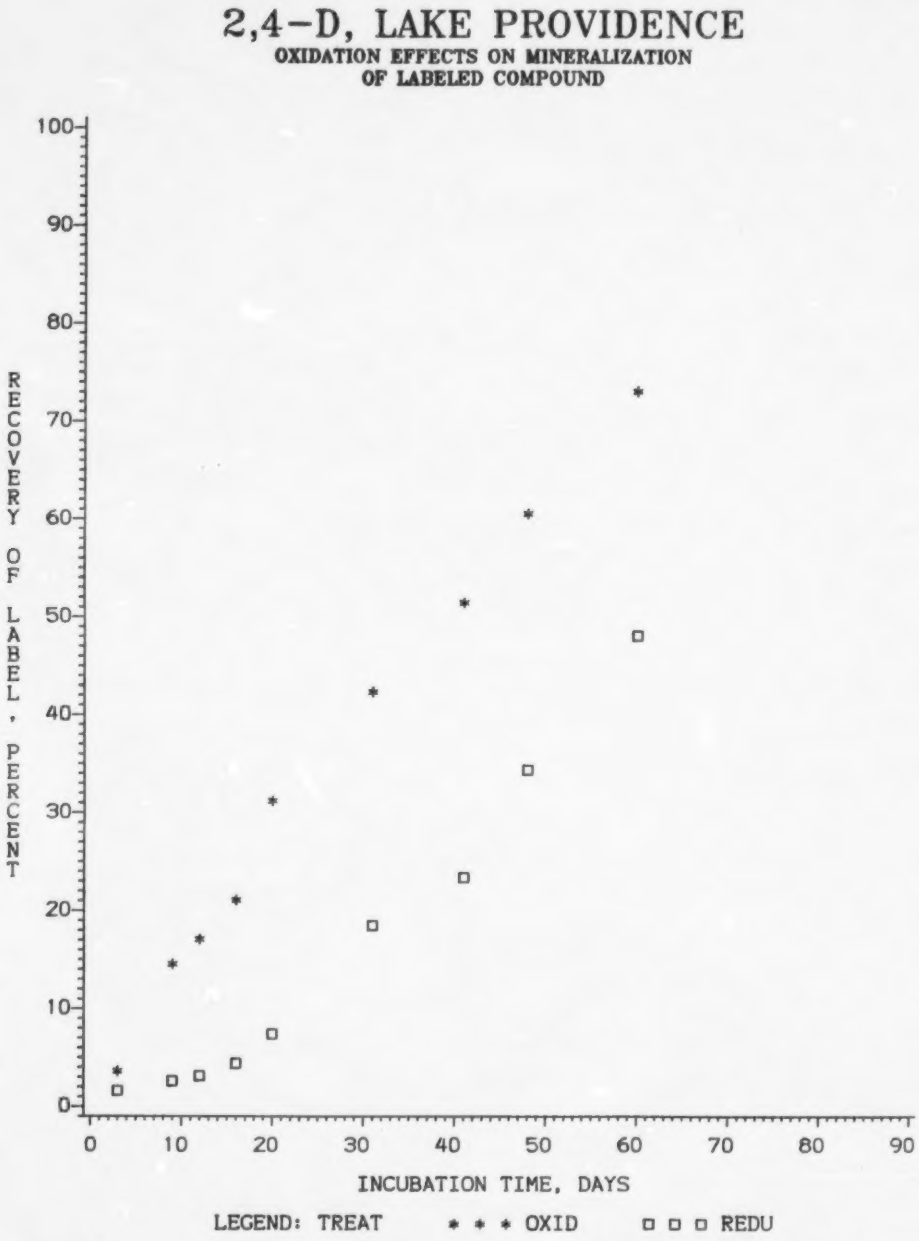

Figure 42. Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Lake Providence sediment material.

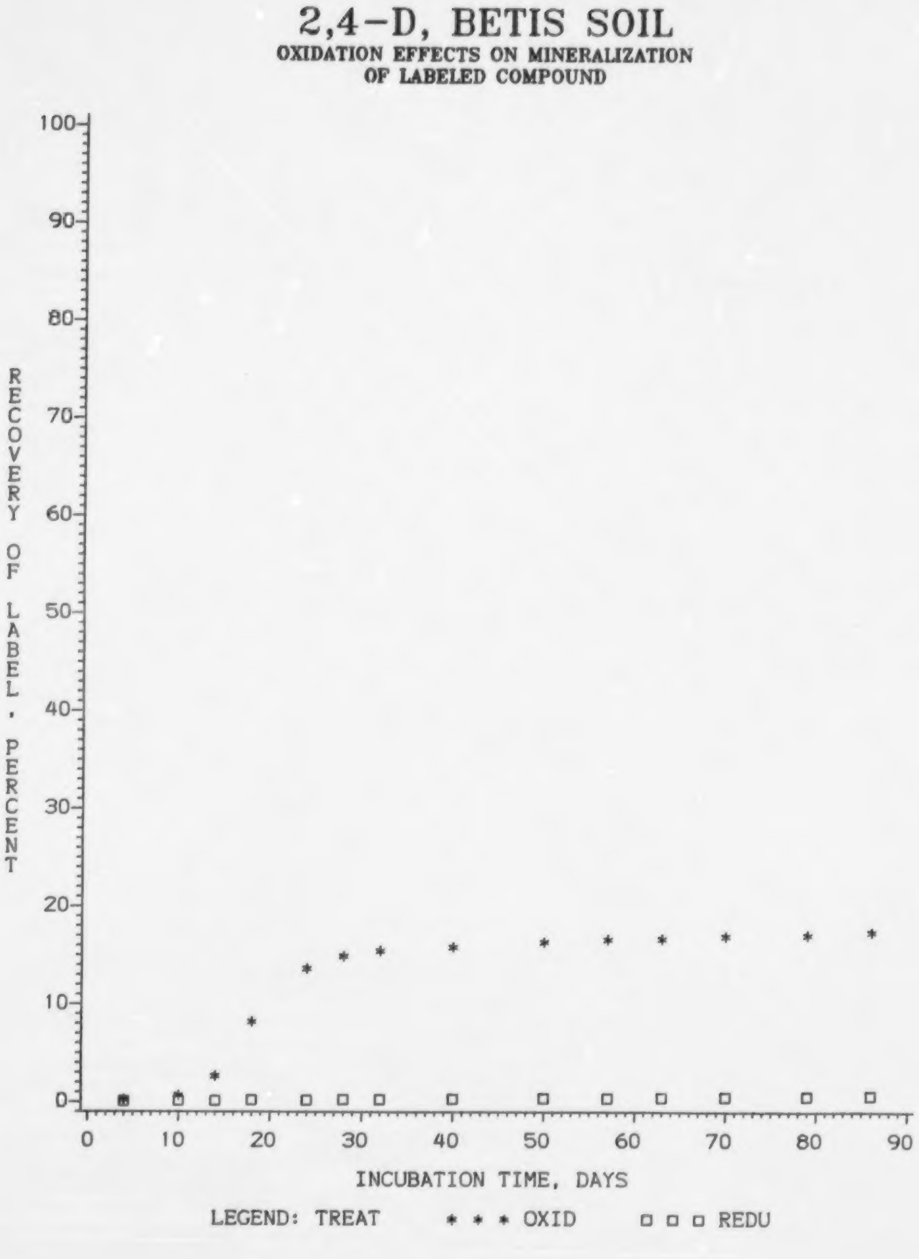

Figure 43. Oxidation effects on degradation of labeled 2,4-D as indicated by recovery of $^{14}CO_2$ from moist, unstirred Betis topsoil material.

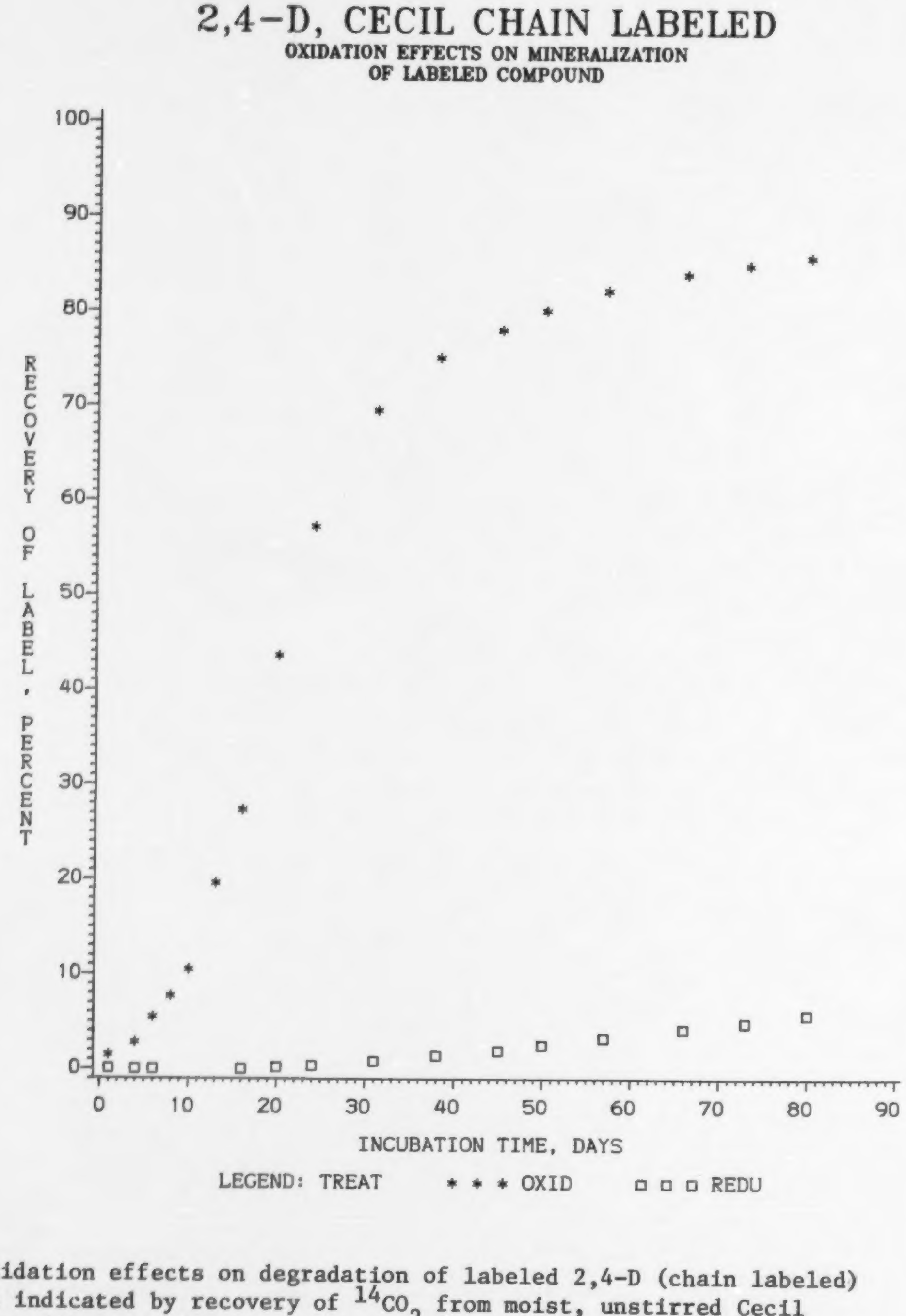

Figure 44. Oxidation effects on degradation of labeled 2,4-D (chain labeled) as indicated by recovery of $^{14}CO_2$ from moist, unstirred Cecil topsoil material.

labeled carbon as carbon dioxide occurs only after substantial modification of the molecule, probably involving several intermediates.

All of the biometer flask 2,4-D degradation results presented to this point have used ring-labeled 2,4-D. Figure 44 gives the recovery of labeled carbon dioxide from chain labeled 2,4-D incubated in a Cecil topsoil material. It was observed that the rate of mineralization of the ring and side chain organic units were essentially the same.

ADSORPTION STUDIES

Adsorption of Methyl Parathion and 2,4-D by 19 Soil and Sediment Materials

The physical and chemical properties of the soil and sediment materials studied are given in Table 2. Adsorption/desorption coefficients for methyl parathion equilibrated with the 19 soils and sediments are given in Table 7. Distribution coefficients were calculated for 2 hrs and 24 hrs adsorption. Soils 1, 3, 4, 7, 11, 14, and 15 adsorbed methyl parathion relatively strongly after a 2 hr equilibration and soils 2, 5, 9, 18, and 19 did not strongly adsorb this compound. Those soils that adsorbed relatively strongly were generally those with the highest organic matter content and those in the group that weakly adsorbed tended to have the lowest organic matter contents. The adsorption coefficients were generally about the same or slightly higher after 24 hrs equilibration for most of the soils tested compared to the 2 hr equilibration except for the muck which adsorbed substantially more at 24 hrs. Distribution coefficients of 2,4-D are presented in Table 8. The values in the table showed the same trend from soil to soil as methyl parathion except that the coefficients were less indicating 2,4-D is less tightly bound than methyl parathion. The data show that with the exception of the Shubuta series, adsorption coefficients for 2,4-D were greater as the pH of the soil decreased.

The relationship between sorption and the soil organic carbon content can be expressed by dividing the individual distribution coefficients of the samples by their respective organic carbon contents to produce K_{oc} values (Hamaker and Thompson, 1972; Karickhoff et al., 1979). Calculation of K_{oc} values has the effect of putting the sorption on a uniform organic carbon basis, assuming that all the organic carbon is equally effective (Lambert, 1968) in sorbing methyl parathion and 2,4-D. The methyl parathion K_{oc} values obtained for all samples investigated in this research ranged from 466 to 2815 and 554 to 2831 for 2 hrs and 24 hrs adsorption respectively with average values of 1374 and 1516 respectively (Table 9).

The K_{oc} values for 2,4-D were also lower than for methyl parathion ranging from 9 to 330 and 40 to 415 for 2 hrs and 24 hrs adsorption, respectively with an average value of 93 and 160 respectively. The substantially decreased coefficients of variation [(S/x) x 100] of K_{oc} values compared to coefficients of variation of adsorption coefficients for both compounds indicates the reduced variability between soils when adsorption is considered on an organic carbon basis (Table 10). This supports what others have reported in the literature.

TABLE 7. DISTRIBUTION COEFFICIENTS FOR METHYL PARATHION EQUILIBRATED WITH 19 SOIL AND SEDIMENT MATERIALS

Soil material	KA[*]	KB[**]
1. Airplane Lake[1]	70.63±0.30[¶]	64.21±0.58[¶]
2. Atchafalaya River[1]	2.03±0.08	2.52±0.07
3. Bayou Chevreuil[1]	60.85±0.56	64.15±0.40
4. Calcasieu River[1]	56.35±1.40	49.28±1.17
5. Cecil Subsoil	2.58±0.12	4.62±0.52
6. Cecil Topsoil	16.17±0.09	23.36±0.65
7. Chastain	39.58±0.98	48.94±0.39
8. Crowley	21.78±0.26	19.53±0.11
9. Gallion	3.46±0.14	3.85±0.13
10. Hartwell Lake[1]	18.16±0.10	20.32±0.11
11. Lafitte Muck	79.93±3.69	251.41±8.93
12. Lake Pontchartrain[1]	14.08±0.59	15.57±0.91
13. Lake Providence	18.77±0.93	20.40±0.63
14. Leeville	50.48±3.92	40.17±2.05
15. Loring	162.45±3.25	153.88±2.59
16. Mhoon	5.80±0.23	7.54±0.14
17. Mississippi River[1]	23.32±0.54	24.54±0.45
18. Norwood	2.69±0.12	3.10±0.09
19. Shubuta	2.05±0.12	3.13±0.19
Mean ($\bar{x}$)	34.3	43.2
Standard deviation(s)	39.9	61.8
Coefficient of variation (CV, %)	114	143

[*] KA: 2-hour adsorption coefficient

[**] KB: 24-hour adsorption coefficient

[1] Sediment

[¶] Mean of triplicate subsamples and standard deviation

TABLE 8. DISTRIBUTION COEFFICIENTS FOR 2,4-D EQUILIBRATED WITH 19 SOIL AND SEDIMENT MATERIALS

Soil material	KA[*]	KB[**]
1. Airplane Lake[1]	0.85±0.05[¶]	1.52±0.06[¶]
2. Atchafalaya River[1]	0.16±0.07	0.67±0.05
3. Bayou Chevreuil[1]	0.69±0.07	1.37±0.01
4. Calcasieu River[1]	1.42±0.11	1.89±0.07
5. Cecil Subsoil	0.69±0.04	1.31±0.08
6. Cecil Topsoil	0.83±0.04	1.67±0.12
7. Chastain	8.45±0.13	10.85±0.09
8. Crowley	0.50±0.07	0.93±0.06
9. Gallion	0.33±0.07	0.87±0.08
10. Hartwell Lake[1]	3.75±0.10	4.46±0.07
11. Lafitte Muck	20.16±0.24	39.09±0.67
12. Lake Pontchartrain[1]	1.82±0.08	2.28±0.07
13. Lake Providence[1]	0.19±0.09	0.85±0.05
14. Leeville	1.29±0.02	1.93±0.09
15. Loring	8.96±0.31	9.99±0.11
16. Mhoon	0.05±0.08	0.38±0.05
17. Mississippi River[1]	0.51±0.03	1.17±0.08
18. Norwood	0.31±0.07	0.70±0.04
19. Shubuta	0.09±0.02	0.44±0.03
Mean ($\bar{x}$)	2.7	4.3
Standard deviation(s)	5.0	8.9
Coefficient of variation (CV, %)	185	206

[*] KA: 2-hour adsorption coefficient

[**] KB: 24-hour adsorption coefficient

[1] Sediment

[¶] Mean of triplicate subsamples and standard deviation

TABLE 9. PERCENT ORGANIC CARBON AND DISTRIBUTION COEFFICIENTS ON AN ORGANIC CARBON BASIS FOR METHYL PARATHION AND 2,4-D IN 19 SOIL AND SEDIMENT MATERIALS

Soil material	% OC	Methyl parathion		2,4-D	
		2 hrs adsorption K_{oc}	24 hrs adsorption K_{oc}	2 hrs adsorption K_{oc}	24 hrs adsorption K_{oc}
1. Airplane Lake[1]	3.80	1859	1690	22	40
2. Atchafalaya River[1]	0.24	846	1050	67	279
3. Bayou Chevreuil[1]	3.44	1769	1865	20	40
4. Calcasieu River[1]	2.30	2450	2143	62	82
5. Cecil Subsoil	0.43	600	1074	160	305
6. Cecil Topsoil	1.67	968	1399	50	100
7. Chastain	2.99	1324	1637	283	363
8. Crowley	2.16	1008	904	23	43
9. Gallion	0.51	678	755	65	171
10. Hartwell Lake[1]	1.91	951	1064	196	234
11. Lafitte Muck	15.45	517	1627	130	253
12. Lake Pontchartrain[1]	0.55	2560	2831	330	415
13. Lake Providence[1]	1.53	1227	1333	12	56
14. Leeville	2.02	2499	1989	64	96
15. Loring	5.77	2815	2667	155	173
16. Mhoon	0.54	1074	1396	9	70
17. Mississippi River[1]	1.16	2010	2116	44	101
18. Norwood	0.56	480	554	55	125
19. Shubuta	0.44	466	711	20	100
Mean ($\bar{x}$)		1374	1516	93	160
Standard deviation(s)		782	642	93	115
Coefficient of variation (CV, %)		57	42	100	72

---

[1] Sediment

TABLE 10. MEANS, STANDARD DEVIATIONS, AND COEFFICIENT OF VARIATION FOR K AND K_{oc} VALUES OF METHYL PARATHION AND 2,4-D ADSORPTION IN 19 SOIL AND SEDIMENT MATERIALS

Compound	Equilibration time, hr	Parameter	$\bar{x}$	s	CV
methyl parathion	2	K	34.3	39.9	116
methyl parathion	2	K_{oc}	1374	782	57
methyl parathion	24	K	43.2	61.8	143
methyl parathion	24	K_{oc}	1516	642	42
2,4-D	2	K	2.7	5.0	185
2,4-D	2	K_{oc}	93	93	100
2,4-D	24	K	4.3	8.9	207
2,4-D	24	K_{oc}	160	115	72

Table 11 gives the results of a statistical analysis to determine R^2 values, the amount of variability in a dependent variable that is explained by the variation in one or more independent variables. Where all 19 soil and sediment materials were included, organic matter content gave the highest R^2 values (except for methyl parathion with a 2 hr adsorption period). Soil pH and cation exchange capacity are also reasonably well associated with 2,4-D adsorption where all 19 soils were included, while CEC contributed significantly for methyl parathion. The soil property most often correlated with 2,4-D adsorption is organic matter (Bailey and White, 1964). Our data on 19 soil and sediment materials indicate that low pH also promotes 2,4-D adsorption.

In soil and sediment materials where the organic matter content is very low, other soil properties may then become substantially more important in regulating the mobility of synthetic organics. One objective of this work was to examine the importance of properties other than organic matter content in adsorbing these pesticides in materials with low organic matter content. In particular, we were interested in examining the role of reducible iron levels as well as the Al extracted by an ammonium oxalate extractant. Therefore, R^2 values describing the relationship between adsorption and soil properties were also determined on those soil and sediment materials with less than 1% organic carbon.

In these low organic matter materials, pH gave low R^2 values between .31 and .36 for both 2 and 24 hr adsorption coefficients for both compounds and all of the other properties we originally planned to examine gave much lower values. In particular, oxalate extractable Fe and Al levels gave especially low R^2 values. In these low organic matter materials, however, we observed that the relationship between adsorption and oxalate extractable Mn and Ca increased, especially for 2,4-D. Where the best three (1st, 2nd, and 3rd highest R^2 values) models with two independent variables were examined for both equilibration times and both compounds in the low organic matter materials, Mn and Ca appeared in 11 of the 12 pairs and the R^2 values were substantially higher than where the best single independent variables were considered in these low organic matter soils.

Thus in soil and sediment materials with low organic matter content, Ca and Mn or factors associated with weak chelate extractable levels of these elements may be important for regulating the mobility of these synthetic organics.

The Effect of pH and Redox Potential on the Adsorption of Methyl Parathion and 2,4-D

Table 12 gives adsorption coefficients for 2 and 24 hr equilibrations of methyl parathion with five soil and sediment materials that had been incubated under controlled pH and redox potential conditions. Although the adsorption procedure was applied to materials incubated at -150 mv, the data are not included because the degradation studies indicated that most of the added methyl parathion was not recovered within hours of amending the suspensions, thus much of the ^{14}C-labeled material measured in the aqueous phase may not have been the parent compound. Whether or

TABLE 11. R^2 VALUES FOR KA[1] AND KB[2] FOR 2,4-D AND METHYL PARATHION VS. SELECTED INDEPENDENT VARIABLES

			R^2 for single independent variables											
Compound	Dependent parameter	# Soils	Organic matter	Clay	Sand	pH	CEC	Al	Fe	Mn	Ca	Best pair, R^2	2nd best pair, R^2	3rd best pair, R^2
2,4-D	K 2 hr.	19(all)	.84**	.15	.13	.30*	.60**	.26*	.12	.00	.00	pH-OM, .90**	iron-OM, .87**	Al-OM, .85**
2,4-D	K 24 hr.	19(all)	.90**	.10	.07	.22*	.56**	.18	.05	.02	.00	pH-OM, .92**	OM-sand, .91**	Ca-OM, .91**
2,4-D	K 2 hr.	7 (low OM)	.03	.01	.01	.31	.00	.00	.00	.62*	.32	Mn-sand, .82**	Mn-clay, .78**	Mn-Al, .73*
2,4-D	K 24 hr.	7 (low OM)	.02	.04	.00	.34	.00	.02	.03	.66*	.40	Mn-sand, .84**	Mn-clay, .77**	Mn-CEC, .74**
methyl parathion	K 2 hr.	19(all)	.34**	.17	.26*	.08	.46**	.16	.14	.02	.00	iron-CEC, .47**	Mn-CEC, .47**	CEC-sand, .47**
methyl parathion	K 24 hr.	19(all)	.93**	.14	.15	.17	.70**	.18	.07	.00	.00	CEC-OM, .93**	OM-clay, .93**	iron-OM, .93**
methyl parathion	K 2 hr.	7 (low OM)	.10	.07	.16	.32	.03	.07	.06	.15	.08	Ca-clay, .74**	Ca-Al, .68**	Mn-sand, .53
methyl parathion	K 24 hr.	7 (low OM)	.11	.03	.12	.36	.01	.02	.02	.17	.14	Ca-clay, .74**	Ca-Al, .66**	iron-Ca, .50

[1] 2-hour adsorption coefficient

[2] 24-hour adsorption coefficent

**Significant at 1% level

*Significant at 5% level

TABLE 12. ADSORPTION COEFFICIENTS FOR METHYL PARATHION IN SOIL AND SEDIMENT MATERIALS INCUBATED UNDER CONTROLLED PH AND REDOX POTENTIAL CONDITIONS

		pH 7.0			pH 5.0		
		Redox potential, mv			Redox potential, mv		
Soil Material	Adsorption Coefficient	50	250	500	50	250	500
Hartwell Reservoir sediment	K_A[1]	18.49 ± 0.04	19.98 ± 0.21	18.97 ± 0.20	17.07 ± 0.43	22.00 ± 0.69	21.97 ± 0.48
	K_B[2]	22.08 ± 0.42	26.24 ± 0.64	22.87 ± 0.34	21.25 ± 0.27	27.87 ± 0.16	28.12 ± 0.67
Cecil clay loam	K_A	34.69 ± 0.86	25.90 ± 0.45	22.87 ± 1.36			
	K_B	39.52 ± 1.61	30.38 ± 0.26	25.91 ± 0.27			
Lake Providence sediment	K_A	21.66 ± 0.54	19.49 ±12.64	26.27 ± 1.49	32.36 ± 0.27	33.39 ± 0.28	40.36 ± 0.26
	K_B	25.84 ± 0.46	20.11 ±12.58	28.68 ± 1.89	33.80 ± 0.23	36.35 ± 0.33	42.84 ± 0.68
Crowley silt loam	K_A	5.06 ± 0.32	4.56 ± 0.33	6.50 ± 1.65	6.45 ± 0.16	5.86 ± 0.57	5.34 ± 0.49
	K_B	6.10 ± 0.23	5.80 ± 0.63	7.73 ± 1.78	8.20 ± 0.20	6.49 ± 0.32	6.95 ± 0.47
Airplane Lake sediment	K_A	74.35 ± 0.15	74.33 ± 3.07	66.89 ± 1.99	92.21 ± 1.29	134.32 ± 2.47	118.46 ± 10.63
	K_B	75.56 ± 0.18	80.91 ± 0.84	72.05 ± 5.55	98.39 ± 5.29	145.64 ± 1.78	138.33 ± 5.25

---

[1] 2-hour adsorption coefficient

[2] 24-hour adsorption coefficient

not rapid modification of methyl parathion occurred in strongly reduced soil materials subject to air drying and grinding prior to equilibration with the adsorbate is not known, but until this possibility is checked, the -150 mv data should not be included.

In the four soil materials where adsorption studies were done at two pH levels (7.0 and 5.0), there tended to be more adsorbed at the lower pH. Only 4 of 24 measurements at pH 5.0 for which there were corresponding values at pH 7.0 gave a lower adsorption coefficient at pH 5.0, and all of these four values were only slightly lower. Adsorption coefficients were lower at +50 mv than higher redox potential values in three of four materials at pH 5.0, but there were no consistent redox potential effects apparent over all soil materials at both pH levels.

In the highly organic Airplane Lake sediment at pH 5.0, there did appear to be an increase in adsorption as redox potential increased above 50 mv.

Two- and 24-hour adsorption coefficients for 2,4-D under different redox potential conditions are given in Table 13 for four soil materials at pH 5.0 and five soil materials at pH 7.0. In three of the four soil materials for which data are available at both pH levels, adsorption was greater at pH 5.0 than 7.0. As for methyl parathion, there was no general redox potential effect apparent over all soils. However, as noted for methyl parathion, both pH and redox potential may have substantially affected adsorption in the highly organic Airplane Lake sediment where 2,4-D was much more strongly adsorbed under oxidized conditions at pH 5.0 than under any other combination of experimentally imposed conditions.

The Effect of Redox Potential and Sample Processing Methods on the Adsorption of Pentachlorophenol

The results of the adsorption/desorption study using PCP and Shell Beach sediment material incubated under oxidized and reduced conditions is given in Table 14. It is apparent that a 2-hour shaking period did not give adequate time for the adsorption process to equilibrate as the distribution coefficient (K) was greater after 24 hours than two hours in every case.

Regardless of the sample processing technique used, the data indicate PCP was more tightly bound to oxidized sediment solids than to reduced sediments. Thus there would be some tendency for PCP in a contaminated sediment-water system to preferentially become associated with the thin oxidized, surface sediment horizon as well as suspended colloidal particulates, which would also tend to be oxidized. Preferential adsorption to suspended particulates in predominantly oxidized, shallow coastal waterbodies could also favor transport from contaminated areas, but would also result in enhanced degradation since degradation was shown to be faster in oxidized Shell Beach sediment-water systems (DeLaune, Gambrell, and Reddy, 1983).

The relatively soluble nature of PCP is indicated by the fact that sediment materials in the presence of uncontaminated water may desorb

TABLE 13. ADSORPTION COEFFICIENTS FOR 2,4-D IN SOIL AND SEDIMENT MATERIALS INCUBATED UNDER CONTROLLED PH AND REDOX POTENTIAL CONDITIONS

Soil Material	Adsorption Coefficient	pH 7.0				pH 5.0			
		Redox potential, mv				Redox potential, mv			
		-150	50	250	500	-150	50	250	500
Hartwell Reservoir sediment	K_A[1]	0.46 ±0.13	0.52 ±0.02	0.18 ±0.14	0.59 ±0.06			1.76 ± 0.05	1.50 ± 0.04
	K_B[2]	1.29 ±0.08	1.48 ±0.27	0.93 ±0.05	1.59 ±0.09			2.67 ± 0.02	2.26 ± 0.24
Cecil clay loam	K_A	0.26 ±0.07	0.20 ±0.02	0.71 ±0.06	0.25 ±0.07				
	K_B	1.25 ±0.01	1.25 ±0.10	1.53 ±0.04	1.24 ±0.06				
Lake Providence sediment	K_A		0.65 ±0.04	0.44 ±0.04	0.88 ±0.06		0.83 ±0.05	1.01 ± 0.14	2.13 ± 0.02
	K_B		1.20 ±0.06	1.08 ±0.04	1.43 ±0.08		1.60 ±0.06	1.79 ± 0.05	2.69 ± 0.05
Crowley silt loam	K_A	0.25 ±0.03	0.45 ±0.03	0.64 ±0.36	0.81 ±0.07	1.21 ±0.12	0.22 ±0.03	0.11 ± 0.01	0.21 ± 0.04
	K_B	0.77 ±0.09	0.92 ±0.10	1.33 ±0.25	2.17 ±1.29	1.79 ±0.06	0.83 ±0.09	0.69 ± 0.02	0.58 ± 0.06
Airplane Lake sediment	K_A	0.84 ±0.08	1.09 ±0.11	1.06 ±0.09	1.18 ±0.04	1.30 ±0.03	2.59 ±0.13	11.94 ± 0.68	13.49 ± 0.32
	K_B	1.60 ±0.11	1.73 ±0.09	1.75 ±0.11	1.86 ±0.03	1.88 ±0.08	3.21 ±0.04	14.93 ± 0.59	16.58 ± 0.43

---

[1] 2-hour adsorption coefficient

[2] 24-hour adsorption coefficient

TABLE 14. ADSORPTION-DESORPTION OF PCP FROM SHELL BEACH SEDIMENT

Method of sediment sample preparation	Oxidation conditions	pH	Distribution coefficients		
			2 hrs adsorption	24 hrs adsorption	2 hrs desorption
			------ 'K' values ------		---- % ---
Not dried[1]	Reduced	6.8	76.76[a3]	117.15[a]	6.39[a]
Not dried	Oxidized	6.8	111.08[b]	169.80[b]	4.49[b]
Dried & ground[2]	Reduced	6.8	31.86[a]	50.67[a]	14.02[a]
Dried & ground	Oxidized	6.8	72.57[b]	105.81[b]	8.38[b]

[1] Wet method: Sediment materials were not dried prior to amending with labeled PCP.

[2] Dry method: Sediment materials dried and ground prior to amending with labeled PCP.

[3] Means within columns for each method of sample preparation not followed by the same letter are significantly different at the 5% level using Duncan's Multiple Range procedure.

several percent of the initially adsorbed PCP into the aqueous phase within two hours. This also suggests that PCP may be relatively mobile in sediment-water systems. The somewhat greater attraction of an oxidized solid phase (sediment or suspended particulates) for PCP and its rapid degradation under oxidized conditions are complimentary processes enhancing the rate of removal from contaminated sediment-water systems.

SECTION 4

SUMMARY AND CONCLUSIONS

PESTICIDE CONCENTRATION EFFECTS ON THE RATE OF SOIL REDUCTION

A simple technique was demonstrated for determining the potential for synthetic organics to stress microbial populations. Oxidized Crowley and Cecil soil materials were amended with varying concentrations of 2,4-D and methyl parathion, flooded, and then analyzed for changes in pH, redox potential, and levels of soluble plus exchangeable Fe, Mn, and Zn, all of which may be directly or indirectly influenced by the activity of soil microorganisms. At the concentrations tested (up to 75 ppm), there was little effect of 2,4-D, but methyl parathion apparently did affect microbial activity contributing to changes in the measured soil properties upon flooding. This approach may be a useful technique for screening various compounds for their potential to stress microbial activity that, for many researchers, would be easier than direct observations of microbial parameters such as population numbers and classifications, or enzyme levels.

DEGRADATION STUDIES

Two types of degradation studies were conducted. In one, soil and sediment materials were maintained under controlled pH and redox potential conditions and amended with either methyl parathion, 2,4-D, or Aroclor 1254. Then the loss of these compounds with time was measured by extraction and gas chromatography analysis as an indication of degradation. In the other type of degradation study conducted, methyl parathion and 2,4-D uniformly labeled with ^{14}C in the aromatic ring were incubated under air and oxygen-free nitrogen conditions in several soil and sediment materials. Collection of labeled carbon dioxide was used as a measure of degradation. These are commonly called biometer flask degradation studies.

Comparing the results of the extraction/gas chromatography studies and the biometer flask studies revealed major differences in the conclusions one might draw on the effects of oxidation conditions on degradation rates. One difference is that the observed degradation rate of methyl parathion is much slower in the unstirred soil and sediment materials (biometer flasks) compared to the stirred suspensions (extraction/gas chromatography analysis). Another more striking difference is that oxidation-reduction treatment effects are opposite for methyl parathion using the two degradation study techniques. These observations must be addressed.

Regarding the rate of degradation, the biometer flasks were maintained at about 23°C whereas the stirred suspensions were kept at about 28°C. The temperature difference would be expected to contribute to some increase in degradation rate in the stirred suspension, but it is unlikely temperature differences accounted for most of the degradation differences observed.

The rate of degradation may be enhanced in stirred suspensions compared to unstirred conditions. Parr and Smith (1974) noted a stirring effect in laboratory studies of toxaphene degradation under both aerobic and anaerobic conditions. It was suggested that stirring some soils provides additional available carbon to microorganisms to sustain rapid degradation of toxaphene. Measurements of total carbon dioxide evolution showed there was a higher level of respiratory activity in a stirred anaerobic suspension compared to a moist, unstirred, anaerobic suspension.

Next, the apparent opposite treatment effects, depending on the type of degradation study, must be addressed. In the biometer flask studies, the labeled carbon was located in the aromatic ring of the methyl parathion molecule. Literature discussed elsewhere in this report suggest that several other modifications to the molecule may occur before degradation of the aromatic ring (i.e., hydrolysis of the ester group and reduction of the nitro group on the benzene ring). Thus recovery of the label as carbon dioxide represents very substantial modification (degradation) of the parent compound. The rate of recovery of the label as carbon dioxide does not say anything about the rate of initial or partial degradation of the parent compound as several sequential intermediate degradation products are probably involved before mineralization of the aromatic ring to carbon dioxide occurs. Thus it is highly probable that modification of the parent molecule occurred at a greater rate than indicated by the rate of recovery of the label. Extraction of the soil or sediment material and analysis by gas chromatography more accurately indicates the rate of loss of the parent compound, but, unless intermediate degradation products are identified and quantified, does not reveal much about the rate of total mineralization of the parent molecule. Both ^{14}C labeled and extraction/specific compound quantification methods are used extensively in degradation studies of synthetic organics. The comparison of results by the two methods in this study which indicate opposite treatment effects clearly indicate a researcher should carefully consider the compatibility of a particular experimental approach with the research objectives.

Controlled pH-Redox Potential Microcosm Studies

The primary purpose of the stirred suspension studies was to determine relative effects of redox potential on the degradation of the three synthetic organics. Continuous stirring insures that uniform conditions are maintained throughout the media.

Salinity effects on the loss of methyl parathion from an estuarine sediment were minimal in this study. Soil and sediment differences, pH, and redox potential levels had a greater effect on the loss of methyl parathion. Sediments tended to give more rapid degradation than soils. In the two materials studied at different pH levels, methyl parathion loss was greater at near neutral pH levels compared to moderately acid conditions. Of the experimental parameters examined, redox potential had the greatest effect on the loss of methyl parathion. Methyl parathion levels decreased much more rapidly under reducing than oxidizing conditions. Generally, there was a sequential increase in degradation rate for every incremental decrease in redox potential over the four Eh levels studied.

The apparent very rapid degradation of methyl parathion under strongly reduced conditions is believed to be due to processes other than direct microbial metabolism as substantial losses and, in one case, a complete loss of the compound was observed within hours. Plots of the log of concentration vs. time were nearly linear as indicated by high correlation coefficients in most cases. However, careful examination of these plots revealed a slight upward curve was present indicating some deviation from first order degradation kinetics.

One degradation study using stirred suspensions and controlled pH and redox potential conditions was conducted with 2,4-D. As observed for methyl parathion, redox potential conditions greatly affected the loss of 2,4-D, but, unlike methyl parathion, 2,4-D was removed much more rapidly from oxidized than reduced soil material.

Aroclor 1254 was incubated at two pH and four redox potential levels for six weeks. Although recovery decreased to about half of initial levels after six weeks in the stirred suspensions, there was no apparent effect of pH or redox potential on the recovery of this PCB formulation.

In selected studies, carbon dioxide production and evolution was measured from mircocosms incubated under controlled redox potential conditions. The data indicate greater microbial activity with increasing redox potential. It was not possible to relate the degradation rate of any of the compounds studied directly to microbial activity levels. With methyl parathion in particular, it is obvious factors and processes other than microbial respiration rates are involved with the rate of degradation.

Biometer Flask Studies

An advantage of using biometer flasks for degradation studies is their simplicity. Compared to the controlled pH-redox potential microcosms, the biometer flasks, using collection of ^{14}C-labeled carbon dioxide as an indication of degradation, permits the study of a larger number of experimental parameters with adequate replication. It should be noted that this experimental method measures mineralization of the labeled portion of the molecule rather than simple modification of the parent compound. How this affects experimental observations in degradation studies compared to extraction/gas chromatography methods is discussed elsewhere in this report.

Carbon-14 labeled methyl parathion was incubated two to three months in six soil and sediment materials under air and nitrogen atmospheres. There was a very large and statistically significant oxidation treatment effect in all six materials. In every case, 10 to 20 or more times of the labeled carbon from the aromatic ring was evolved as labeled carbon dioxide under oxidizing conditions compared to reducing conditions. The observed oxidation treatment effects were opposite the results obtained from the stirred suspension/extraction/analysis by gas chromatography studies for methyl parathion. The reasons for this are discussed elsewhere.

Recovery of the ring-labeled carbon in 2,4-D as carbon dioxide was also much greater under oxidized conditions. For the one soil material studied using both ring- and chain-labeled 2,4-D, no difference was noted in the rate of mineralization of the aromatic ring or the alkyl chain portion of the molecule.

ADSORPTION STUDIES

Methyl Parathion and 2,4-D Adsorption Study Using 19 Soil and Sediment Materials

Adsorption coefficients for 2,4-D and methyl parathion were determined in 19 soil and sediment materials selected to give a wide range in physical and chemical properties. Organic matter content of the materials was generally indicated to be the most important property affecting adsorption. As expected, 2,4-D was less strongly associated with the sediment phase than methyl parathion, and pH was more closely associated with the adsorption of 2,4-D than with methyl parathion.

One objective of this study was to examine soil properties that may be important in immobilizing synthetic compounds where the soil organic matter content is low. Data were presented indicating that in these low organic matter content soils, the association between adsorption and oxalate extractable Mn and Ca may be an important relationship. Additional work should be done in low organic matter soil material to better quantify the relationship between adsorption and soil geochemical properties. As our work has demonstrated, those properties closely associated with the mobility of some synthetic organics in typical surface soils may not be useful in predicting the immobilization of synthetic organics in subsoils. Understanding the relationship between geochemical properties and the mobility of synthetic organics is especially important in typical, low-organic matter subsoil materials that have been contaminated with hazardous organics such as has occurred at many hazardous waste disposal sites.

pH and Redox Potential Effects on Adsorption

Methyl parathion tended to adsorb to the soil materials tested more strongly at pH 5.0 than 7.0. There were no consistent redox potential effects for methyl parathion over all soil materials and pH levels, but in the highly organic Airplane Lake sediment at pH 5.0, adsorption appeared to increase as redox potential increased above 50 mv.

For 2,4-D, adsorption was also greater at pH 5.0 than 7.0 in most soil materials and there was no general redox potential effect over all soils. However, as noted for methyl parathion, both pH and redox potential may have substantially affected adsorption in the highly organic Airplane Lake sediment where 2,4-D was much more strongly adsorbed under oxidized conditions at pH 5.0.

Effects of Oxidation Conditions and Sample Processing Methods on the Adsorption of Pentachlorophenol (PCP)

The method of processing sediment materials prior to conducting the adsorption procedures (testing wet sediment materials vs. aliquots that had been dried and ground) did make a difference in the 2- and 24-hour adsorption coefficients measured. Sample preparation methods did not affect the relative oxidation treatment effects. PCP was more tightly bound to oxidized estuarine sediment solids than to reduced sediment solids.

SECTION 5

RECOMMENDATIONS

Many pesticide and other environmental scientists now recognize that oxidation conditions affect the persistence of synthetic organics in soil and sediment-water systems, though there is relatively little published information on the role of oxidation-reduction conditions on the degradation rate of specific synthetic organics. Where information is available on oxidation-reduction effects on degradation of synthetic organics, the effect of this parameter is usually great enough such that soil and sediment oxidation conditions should be considered in evaluating the persistence and potential impacts of the compounds in the environment. Where suitable information is available, it should be incorporated into modeling efforts to predict the fate of synthetic organics in the environment.

Work done in this laboratory and by a very few other groups has clearly demonstrated the importance of redox potential conditions in soil and sediments on the rate of degradation of many compounds as well as the fact that different compounds respond differently to redox conditions. Unfortunately, the information available to date generally does not provide the information needed to quantify redox potential effects on degradation rates under natural conditions. For example, it appears stirred suspension studies may indicate an artifically high rate of degradation. On the other hand, most degradation studies using carbon-14 labeled compounds in unstirred soil materials make conclusions on degradation rates based on recovery of the labeled carbon as carbon dioxide. In most cases, depending on the molecular structure of the compound and the position of the label, recovery of the label as carbon dioxide certainly indicates the compound has degraded such that nothing of environmental consequence remains. However, this approach tends to be overly cautious as labeled carbon dioxide is collected only after substantial modification of the parent compound, usually through a series of many degradation products. For many compounds, modification of the molecule has proceeded beyond the point where it presents an environmental threat long before the label is recovered as carbon dioxide. Also some of the label, transformed to harmless decomposition products, may be incorporated into the humus fraction of the soil and retained as soil organic matter for extended periods of time. Methods used for degradation studies, particularly those examining physicochemical effects, have been successful in documenting the importance of redox potential, but probably unreliable in indicating effects of physicochemical conditions on the rate of degradation. We have conducted degradation studies using both methods in this project to demonstrate how the experimental approach can affect the results and conclusions of degradation studies. Thus one recommendation coming from this project is that more be done alerting environmental organic chemists doing degradation research to the importance of matching experimental techniques to the research objectives such that erroneous conclusions on treatment effects and degradation rates are minimized.

The sequence of research findings to date have lead to the conclusion that physicochemical conditions do substantially affect the degradation rate of many compounds, but research methods should be devised and employed to provide information on how physicochemical properties of soils and sediments affect the degradation rate of compounds under natural conditions. This information would be most useful to modelers for predicting the persistence of synthetic organics in various environmental compartments. The technique developed should be relatively inexpensive and capable of including a wide range of soil and sediment physical and chemical properties. The experimental material for these degradation studies should be placed in the field where the experimental units are subjected to natural climate, microbial, and hydrologic conditions. Soil and sediment materials should be characterized for most of the commonly measured properties, much as was done in the adsorption study included in this report using 19 soil and sediment materials. One important difference in the degradation studies would be that the soils should be characterized for certain parameters in their natural condition, not after sampling, drying, and grinding. Then degradation rates and soil properties should be evaluated using appropriate statistical procedures to determine the relationship between degradation rate and the measured soil properties. If a large number of soils were included, statistically valid prediction models could be developed for degradation rates under natural conditions based on soil and sediment properties.

LITERATURE CITED

Ahmed, M. K., J. E. Casida, and R. E. Nichols. 1958. Bovine Metabolism of Organophosphorus Insecticides: Significance of Rumen Fluid with Particular Reference to Parathion. J. Agr. Food Chem. 6:740-741.

Ahmed, M., and D. D. Focht. 1973. Oxidation of Polychlorinated Biphenyls of Achromobacter PCV. Bull. Environ. Contam. Toxicol. 10:70-72.

Aly, O. M., and S. D. Faust. 1964. Studies on Fate of 2,4-D and Ester Derivatives in Natural Surface Waters. J. Agr. Food Chem. 12:541-546.

Armstrong, D. E., and D. H. Swackhamer. 1982. Sources of PCBs to Wisconsin Lakes. Water Resources Center, University of Wisconsin, Madison, Wis. (WIS-WRC-82-04) 24 pp.

Audus, L. J. (ed.). 1964. Herbicide Behavior in the Soil. In: The Physiology and Biochemistry of Herbicides. Academic Press, New York, London. pp. 166-203.

Bailey, G. W., and J. L. White. 1964. Soil Pesticide Relationships, Review of Adsorption and Desorption of Organic Pesticides by Soil Colloids with Implications Concerning Pesticide Bioactivity. J. Agr. Food Chem. 12:324-333.

Bell, G. R. 1956. Photochemical Degradation of 2,4-Dichlorophenoxyacetic Acid and the Structurally Related Compounds in the Presence and Absence of Riboflavin. Bot. Gaz. 109:314-323.

Briggs, G. G. 1973. A Simple Relationship Between Soil Adsorption of Organic Chemicals and Their Octanol/Water Partition Coefficients. Proc. 4th British Insec. Fung. Conf. pp. 83-86.

Brown, J. W., and J. W. Mitchell. 1948. Inactivation of 2,4-Dichlorophenoxyacetic Acid in Soil as Affected by Soil Moisture, Temperature, the Addition of Manure, and Autoclaving. Bot. Gaz. 109:314-323.

Carey, A. E., and G. R. Harvey. 1978. Metabolism of Polychlorinated Biphenyls by Marine Bacteria. Bull. Environ. Contam. Toxicol. 20:527.

Chapman, H. D. 1965. Cation Exchange Capacity. In: Methods of Soil Analysis, C. A. Black, ed. Agronomy 9:891-901.

Council for Agricultural Sciences and Technology. 1975. The Phenoxy Herbicides. Weed Sci. 23:259-263.

Crafts, A. A. 1964. Herbicide Behavior in the Plant. In: The Physiology and Biochemistry of Herbicides, L. J. Audus, ed. Academic Press, New York, London. pp. 75-108.

Crafts, A. S. 1960. Evidence for the Hydrolysis of Esters of 2,4-D during Absorption by Plants. Weeds 8:19-25.

Day, P. R. 1965. Particle Fractionation and Particle Size Analysis. In: Methods of Soil Analysis, C. A. Black, ed. Agronomy 9:565-567.

DeLaune, R. D., R. P. Gambrell, and K. S. Reddy. Fate of Pentachlorophenol in an Estuarine Sediment. (submitted for publication).

Eisenreich, S. J., G. J. Hollod, and T. C. Johnson. 1979. Accumulation of Polychlorinated Biphenyls (PCBs) in Surficial Lake Superior Sediments. Atmospheric Deposition. Environ. Sci. Technol. 13:569-573.

Finley, E. L., J. B. Graves, T. A. Summers, P. E. Schilling, and H. F. Morris. 1977. Some Facts about Methyl Parathion Contamination of Clothing in Cotton Fields and Its Removal by Home Laundering. Circular No. 104, Agrl. Expt. Sta., Louisiana State University, Baton Rouge.

Frank, P. A. 1972. Herbicidal Residues in Aquatic Environments. Adv. Chem. Ser. 111:135-148.

Fries, G. P. 1972. Advances in Chemistry Series No. 111. American Chemical Society, Washington, D. C.

Fulk, R. et al. 1975. Laboratory Study of the Release of Pesticide and PCB Materials to the Water Column During Dredging and Disposal Operations. Contract Report D-75-6, U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Gambrell, R. P., R. A. Khalid, M. G. Verloo, and W. H. Patrick, Jr. 1977. Transformations of Heavy Metals and Plant Nutrients in Dredged Sediments as Affected by Oxidation-Reduction Potential and pH. Volume II. Materials and Methods/Results and Discussion. Contract Report D-77-4. U. S. Army Engineers Waterways Experiment Station, Vicksburb, Miss. 39180.

Gibson, R. T. et al. 1973. Oxidation of Biphenyl by a Beijerinckia Species. Biochem. Biophys. Res. Comm. 50:211-219.

Gotoh, S. and W. H. Patrick, Jr. 1972. Transformations of Manganese in Waterlogged Soil as Affected by Redox Potential and pH. Soil Sci. Soc. Am. Proc. 36:738-742.

Gotoh, S. and W. H. Patrick, Jr. 1974. Transformations of Iron in a Waterlogged Soil as Influenced by Redox Potential and pH. Soil Sci. Soc. Am. Proc. 38:66-71.

Graetz, D. A., G. Chesters, T. C. Daniel, L. W. Newland, and G. B. Lee. 1970. Parathion Degradation in Lake Sediments. J. Water Poll. Control Fed. 42:R-76.

Griffin, R. A., A. K. Av, E. S. K. Chian, J. H. Kim, and F. B. DeWalle. 1977. Attenuation of PCBs by Soil Materials and Char Wastes. In: Management of Gas and Leachate in Landfills. EPA-600/9-77-026, pp. 208-217.

Griffin, Robert, Robert Clark, Michael Lee, and Edward Chian. 1978. Disposal of Removal of Polychlorinated Biphenyls in Soil. In David Schultz (ed.) Land Disposal of Hazardous Waste, Fourth Annual Research Symposium, Solid and Hazardous Waste Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45269.

Hamaker, J. W., and J. M. Thompson. 1972. Adsorption. In: Organic Chemicals in the Soil Environment, C. A. I. Goring and J. W. Hamaker, eds. Marcel Dekker, Inc., New York. Chapter 2, pp. 51-143.

Haque, R., and R. Sexton. 1968. Kinetic and Equilibrium Study of the Adsorption of 2,4-Dichlorophenoxyacetic Acid on Some Surfaces. J. Colloid Interface Sci. 7:818-827.

Harris, C. I., and G. F. Warren. 1964. Adsorption and Desorption of Herbicides by Soil. Weeds 12:120-125.

Hartley, G. S. 1960. Physicochemical Aspects of the Availability of Herbicide in Soils. In: Herbicides and the Soil, E. K. Woodford and G. R. Sager, eds. Blackwell Sci. Publ., Oxford, England, pp. 63-78.

Hernandez, T. P., and G. F. Warren. 1950. Some Factors Affecting the Rate of Inactivation and Leading of 2,4-D in Different Soils. Proc. Am. Soc. Hort. Sci. 56:287-293.

Howeler, R. H., and D. R. Bouldin. 1971. The Diffusion and Consumption of Oxygen in Submerged Soil. Soil Sci. Soc. Am. Proc. 35:202208.

Jackson, M. L. 1958. Soil Chemical Analysis. Prentice Hall, Inc., Englewood Cliffs, N.J.

Jackson, M. L. 1967. Soil Chemical Analysis. Prentice Hall of India.

Jensen, H. L., and H. I. Petersen. 1952. Detoxication of Hormone Herbicides by Soil Bacteria. Nature 170:39-40.

Johnsen, R. E. 1973. PCB Newsletter No. 5. U. S. Environmental Protection Agency, Duluth, Minnesota. pp. 14.

Jugsujinda, Aroon. 1975. Growth and Nutrient Uptake by Rice under Controlled Oxidation-Reduction and pH Conditions in a Flooded Soil. Ph.D. Thesis, Louisiana State University, Baton Rouge, Louisiana.

Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Res. 13:241-248.

Khan, A., J. J. Hassett, W. L. Banwart, J. C. Means, and S. G. Wood. 1979. Sorption of Acetophenone by Sediments and Soils. Soil Sci. 128:297-302.

Khan, S. U. 1973. Equilibrium and Kinetic Studies of the Adsorption of 2,4-D and Picloram on Humic Acid. Can. J. Soil Sci. 53:429-434.

Lambert, S. M. 1968. Omega(Ω), [illegible] Useful Index of Soil Sorption Equilibria. J. Agr. Food Chem. 16:340-34[illegible].

Lavy, T. L., F. W. Roetti, and C. R. Fenster. 1973. Degradation of 2,4-D and Atrazine at Three Soil Depths in the Field. J. Environ. Qual. 2:132-137.

Leenheer, J. A., and J. L. Ahlrichs. 1971. A Kinetic and Equilibration Study of the Adsorption of Carbaryl and Parathion Upon Soil Organic Matter Surfaces. Soil Sci. Soc. Am. Proc. 35:700-705.

Lichtenstein, E. P., and K. Schulz. 1964. The Effects of Moisture and Microorganisms on the Persistence and Metabolism of Some Organophosphorus Insecticides in Soil with Special Emphasis on Parathion. J. Econ. Entomol. 57:618-627.

Liu, Dickson, William M. J. Strachan, Karen Thomson, and Kazimiera Kwasniewska. 1981. Determination of the Biodegradability of Organic Compounds. Environ. Sci. Technol. 15:788-793.

Loos, M. A. 1969. Phenoxyaltanoic Acids. In: Degradation of Herbicides, P. C. Kearney and D. D. Kaufman, eds. Marcel Dekker, Inc., New York. Chapter 1.

Luchini, L. C., K. A. Lord, and E. F. Ruegg. 1981. Sorption and Desorption of Pesticides on Brazilian Soils. Cienciae Cultura 33(1):97-101.

McKeague, J. A., and J. H. Day. 1966. Dithionite- and Oxalate-Extractable Fe and Al as Aids in Differentiating Various Classes of Soils. Can. J. Soil Sci. 46:13-22.

Miller, R. W., and S. D. Faust. 1972. Sorption from Aqueous Solutions by Organic Clays: I. 2,4-D by Bentone 24. Adv. Chem. Ser. 111:121-134.

Miyamoto, J., K. Kitagawa, and Y. Sato. 1966. Metabolism of Organophosphorus Insecticides by *Bacillus subtilis*, with Special Emphasis on *Sumithion*. Jap. J. Exp. Med. 36:211-225.

Newman, A. S., J. R. Thomas, and R. L. Walker. 1952. Disappearance of 2,4-Dichlorophenoxyacetic Acid from Soil. Soil Sci. Soc. Am. Proc. 16:21-24.

Nicholson, H. P., H. J. Webb, G. J. Laver, R. E. O'Brien, A. R. Grzenda, and D. W. Shariklin. 1962. Insecticide Contamination in a Farm Pond. Trans. Am. Fish. Soc. 91:213-222.

Ogle, R. E., and G. F. Warren. 1954. Fate and Activity of Herbicides in Soils. Weeds 3:257-278.

Paris, Doris F., William C. Steen, and Lawarence A. Burns. 1982. Microbial Transformation Kinetics of Organic Compounds. *In* O. Hutzinger (ed.) *The Handbok of Environmental Chemistry, Volume 2/Part B*. Springer-Verlag, Berlin, Heidelberg, New York, pp. 73-81.

Parr, J. F., and S. Smith. 1974. Degradation of Toxaphene in Selected Anaerobic Soil Environments. Soil Sci. 121:52-57.

Patrick, W. H., Jr., and D. S. Mikkelsen. 1971. Plant Nutrient Behavior in Flooded Soil. In: Fertilizer Technology and Use, R. C. Dinauer, ed. Soil Sci. Soc. Am., Madison, Wisconsin, 2nd Edition.

Patrick, Z. A. 1971. Phytotoxic Substances Associated with the Decomposition in Soil of Plant Residues. Soil Sci. 111:13-18.

Peech, M. 1965. Hydrogen Ion Activity. In: Methods of Soil Analysis, C. A. Black, ed. Agronomy 9:914-926.

Perdue, Edward M., and N. Lee Wolfe. 1982. Modification of Pollutant Hydrolysis Kinetics in the Presence of Humic Substances. Environ. Sci. Technol. 16:847-852.

Rajaram, K. P., and N. Sethunathan. 1975. Effect of Organic Sources on the Degradation of Parathion in Flooded Alluvial Soil. Soil Sci. 119:296-300.

Rajaram, K. P., and N. Sethunathan. 1976. Factors Inhibiting Parathion Hydrolysis in Organic Matter-Amended Soil under Flooded Conditions. Plant and Soil 44:683-690.

Rao, A. V., and N. Sethunathan. 1974. Degradation of Parathion by *Penicillium waksmani* Zaleski Isolated from Flooded Acid Sulphate Soil. Arch. Microbiol. 97:203-208.

Sayler, G. S., R. Thomas, and R. R. Colwell. 1978. Polychlorinated Biphenyl (PCB) Degrading Bacteria and PCB in Estuarine and Marine Environments. Est. Coastal Mar. Sci. 6:553-567.

Sethunathan, N. 1973a. Degradation of Parathion in Flooded Acid Soils. J. Agr. Food Chem. 21:602-604.

Sethunathan, N. 1973b. Microbial Degradation of Insecticides in Flooded Soil and in Anaerobic Cultures. Residue Reviews 47:143-165.

Sethunathan, N. 1973c. Organic Matter and Parathion Degradation in Flooded Soil. Soil Biol. Biochem. 5:641-644.

Sethunathan, N., and T. Yoshida. 1972. Conversion of Parathion to Para-Nitrophenol by Diazinon-Degrading *Flavobacterium sp*. Proc. 18th Ann. Meeting Inst. Environ. Sci. 18:255-357.

Sethunathan, N., and T. Yoshida. 1973. A Flavobacterium sp. That Degrades Diazinon and Parathion. Can. J. Microbiol. 19:873-875.

Sherwood, M. J. 1976. Fin Erosion Disease Induced in the Laboratory. In: Coastal Water Research Project Annual Report; Southern California Coastal Water Research Project. pp. 149-153.

Shiaris, M. P., and G. S. Sayler. 1982. Biotransformation of PCB by Natural Assemblages of Freshwater Microorganisms. Environ. Sci. Technol. 16:367-369.

Stevenson, F. J. 1972. Role and Function of Humus in Soil with Emphasis on Adsorption of Herbicides and Chelation of Micronutrients. Bioscience 22:643-650.

Stewart, D. K., R. D. Chisholm, and T. H. Ragab. 1971. Long Persistence of Parathion in Soil. Nature 229:47.

Suffet, I. H., and S. D. Faust. 1972. The P-Value Approach to Quantitative Liquid-Liquid Extraction of Pesticides from Water. 1. Organophosphates: Choice of pH and Solvent. J. Agr. Food Chem. 20:52-56.

Tucker, E. S. et al. 1975. Activated Sludge Primary Biodegradation of Polychlorinated Biophenyls. Bull. Environ. Contam. Toxicol. 14:705-713.

Veight, G. D. 1970. Environmental Chemistry of the Chlorobiphenyls in the Milwaukee River. Ph.D. Dissertation, University of Wisconsin, Madison.

Wahid, P. A., C. Ramakrishna, and N. Sethunathan. 1980. Instantaneous Degradation of Parathion in Anaerobic Soils. J. Environ. Qual. 9:127-130.

Wahid, P. A., and N. Sethunathan. 1978. Sorption-Desorption of Parathion in Soils. J. Agr. Food Chem. 26:101-105.

Walker, W. W. 1976. Chemical and Microbiological Degradation of Malathion and Parathion in an Estuarine Environment. J. Environ. Qual. 5:210-216.

Wauchope, R. D. 1978. The Pesticide Content of Surface Water Draining from Agricultural Fields - A Review. J. Environ. Qual. 7:459-472.

Weber, J. B. 1970. Behavior of Herbicides in Soils. Proc. Beltwide Cotton Production. Mechanization Conference, Houston, Texas.

Weber, J. B. 1972. Interaction of Organic Pesticides with Particulate Matter in Aquatic and Soil Systems. Adv. Chem. Ser. 111:55-120.

Weber, J. B., P. W. Perry, and R. P. Upchurch. 1965. The Influence of Temperature and Time on the Adsorption of Paraquat, Diquat, 2,4-D, and Prometone by Clays, Charcoal, and an Anion-Exchange Resin. Soil Sci. Soc. Am. Proc. 29:678-688.

Wershaw, R. L., and M. C. Goldberg. 1972. Interaction of Organic Pesticides with Natural Organic Polyectrolytes. Adv. Chem. Ser. 111:149-158.

White, A. W., Jr., L. E. Asmussen, E. W. Hauser, and J. W. Turnbull. 1976. Loss of 2,4-D in Runoff from Plots Receiving Simulated Rainfall and from a Small Agricultural Watershed. J. Environ. Qual. 5:487-490.

Wiese, A. F., and A. G. Davis. 1964. Herbicide Movement in Soil with Various Amounts of Water. Weeds 12:101-103.

Wolfe, N. Lee, Richard G. Zepp, Doris F. Paris, George L. Baughman, and Reginald C. Hollis. 1977. Methoxychlor and DDT Degradation in Water: Rates and Products. Environ. Sci. Technol. 11:1077-1081.

Wong, P. T. S., and K. L. E. Kaiser. 1974. Bacterial Degradation of Polychlorinated Biphenyls. II. Rate Studies. Bull. Environ. Contam. Toxicol. 13:249-256.

Yaron, B. 1978. Some Aspects of Surface Interactions of Clays with Organophosphorus Pesticides. Soil Sci. 125:210-216.

Zuckerman, B. M., K. Deubert, M. Mackiewicz, and H. Gunner. 1970. Studies on the Biodegradation of Parathion. Plant and Soil 33:273-281.